ISOMERIZATION
OF PURE HYDROCARBONS

By

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Dedicated to

COLONEL MARSTON T. BOGERT

with deep appreciation

INTRODUCTION

American Chemical Society [illegible]

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New York.

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to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

Preface

Because of its wide ramifications, isomerization is one of the most important reactions in all chemistry. The present study therefore has been confined to pure hydrocarbons of the aliphatic, alicyclic, and aromatic series. The isomerization of alkanes has developed great value from the scientific as well as the industrial standpoint. During 1941, crude oil production of the world will be over 2,000,000,000 barrels. Most of the alkanes present in the gasoline fraction are of straight-chain character, unsuitable as fuel for modern motor cars or airplanes, as they are too low in octane rating. These alkanes should be isomerized to branch-chain hydrocarbons of high antiknock properties.

One of the key hydrocarbons for the production of 100 or higher octane gasoline is isobutane, which alkylates readily with alkenes, forming isomers of heavier hydrocarbons. In natural and refinery gases the proportion of isobutane to normal averages about thirty per cent. The availability of alkenes from thermal and catalytic cracking for alkylation purposes is far greater than that of isobutane. The isomerization of *n*-butane into isobutane has developed commercially in order to supply the demand for this compound in the production of alkylate gasoline of high octane rating. The alkylates are used for blending with lower grade gasoline and tetraethyllead to produce 100 octane and higher aviation gasoline for the fighting and bombing planes of the United States and Great Britain. The United States production of this quality gasoline for 1941 is estimated at 765,000,000 gallons.

The isomerization of alkenes has industrial importance, such as the conversion of butene into isobutene and the polymerization of the latter to isoöctene motor fuel, viscous oils, or synthetic rubber. Isomerization of hydrocarbons also finds applications in the pharmaceutical, essential oil, perfume, and other industries outside of the petroleum field.

Important as the isomerization reaction is, no single theory or combination of theories adequately covers hydrocarbons. The isomerization of aliphatic hydrocarbons has made potentially available many derivatives, such as alcohols, halides, and esters.

The available experimental data have been calculated to a uniform basis wherever possible. These were thought to be of value for the purpose of comparing catalyst concentration, time, temperature, pressure, and yield of products for more than 1700 experiments on isomerization shown in thirty-six tables.

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Gustav Egloff

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CHAPTER V. CYCLENES, BICYCLENES, AND POLYCYCLENES

Introduction

The hydrocarbons are assuming ever growing importance in many fields of human endeavor. Consequently, more and more emphasis will be placed upon their structures and processes of obtaining selected individual hydrocarbons. Many experiments have been conducted to change the configuration of available hydrocarbons into more desirable types. Isomerization—a fundamental molecular transformation—effects these changes without altering the number of atoms present in the molecule. This reaction has not only scientific but commercial importance in the petroleum, pharmaceutical, essential oil, perfume, and various other industries. Isomerization ramifies through the entire field of organic chemistry; hence this monograph is necessarily limited to hydrocarbons as starting materials and final products. The present study covers the isomerizations of hydrocarbons belonging to the alkane, alkene, alkyne, cyclane, cyclene, mononuclear aromatic, and polynuclear series. It endeavors to give both the qualitative and quantitative aspects of thermal and catalytic isomerizations.

Isomerization is a shift in the configuration of a molecule, without change in the number of atoms present. The formation of isomers from hydrocarbons by isomerization involves: transformations involving single, double, or triple bonds; migrations of aliphatic, alicyclic or aromatic groups; and migration or transfer of hydrogen in the molecule. There are three main classes of hydrocarbon isomerization: structural, geometrical, and optical.

Structural isomerization is the development of isomers by a formation, shifting, modification, or removal of structural units in the molecule, without change in weight. The units operated upon comprise any main aliphatic chain, its branches, all rings, their side-chains, or the unsaturated bonds located in any of these. Structural isomerization includes many complex transformations, or inter-group isomerizations, wherein the isomer product belongs to a different group. The alkanes apparently isomerize only by exchange of methyl groups for hydrogen atoms in the same molecule. Alkenes isomerize by the same transformation, by shift of the double bond, or by *cis-trans* conversion. Cyclizations of alkenes into cyclanes are seldom encountered. Alkadienes isomerize by shifts of their double bonds, by formation of an alkyne, or by cyclization. Alkapolyenes have a great tendency to cyclize. Alkynes isomerize by triple-bond shift or by formation of alkadienes. Cyclanes may revert into

alkenes, change their ring-size, or redistribute their side-chains. Cyclenes are able to shift their double bond about the ring or into a side-chain. If unsaturated side-chains are attached to a cyclene, changes such as conversions into a cyclodiene, a cyclotriene (aromatization), or into a bicyclic isomer occur. The aromatics readily shift unsymmetrically located saturated side-chains. Unsaturated side-chains about various aromatic nuclei are transformed in the manner which is characteristic of unsaturated aliphatic hydrocarbons. Cyclization by closure of an unsaturated side-chain upon the aromatic nucleus is apparently aided by a facile labilization of hydrogen atoms attached to the aromatic rings. The structural isomers in general are different from the geometrical and optical "stereoisomers."

Geometrical isomerization ("*cis-trans* isomerization") is the formation of isomers having different geometrical arrangement of intact groups in the space about points of attachment where free rotation is hindered. Geometrical isomerization among the alkenes takes place under the influence of heat, sunlight, ultraviolet light, or hot acids, or upon "aging." * Cyclic hydrocarbons with hindered rotation of groups about ring carbon-atoms undergo geometrical isomerization upon the application of heat, aided by such catalysts as aluminum chloride, iodine, or nickel.

Optical isomerization is the formation of an isomer with opposite optical rotation. Optical isomerization proceeds during heating of the individual *d*- or *l*-forms. This type of isomerization, in its typical form "inversion," produces a mixture containing equal quantities of the antipodes and exhibiting a statistical optical inactivity. Such racemic mixtures can be resolved subsequently by special processes. An "asymmetrical synthesis," wherein a structurally inactive hydrocarbon forms but one optically active isomer, is generally not encountered in optical isomerization. However, optical isomers may readily isomerize to structurally inactive hydrocarbons. Optical isomers and most of the geometrical isomers, on account of structural similarity, are distinguishable only by their physical properties.

In the study of isomerization, the conditions under which the reaction proceeds deserve great consideration. In many operations of organic chemistry, isomerization results in the formation of isomers which may or may not be desirable, and facilities for controlling the process in this regard should be available. The factors affecting isomerization include: the physical states (gas, liquid, or solid) and concentrations of the initial and final hydrocarbons, concentrations and types of catalysts and sol-

* Throughout this monograph, the word "aging" is used to signify an isomerization that proceeds upon mere standing and which is presumably due to the ordinary thermal agitation of molecules.

vents, rate of reaction (contact time), temperature, pressure, agitation, irradiation, heat of activation, heat of isomerization, and free energy change. Additional factors to be considered in commercial practice are availability and cost of the initial hydrocarbon, cost and recovery of catalysts and inhibitors, and cost and yield of the isomer product.

Very little work has been done on the effect of physical states upon the course of isomerization. The formation and recovery of an isomer product may be facilitated by such operations as sublimation, distillation, and evaporation.

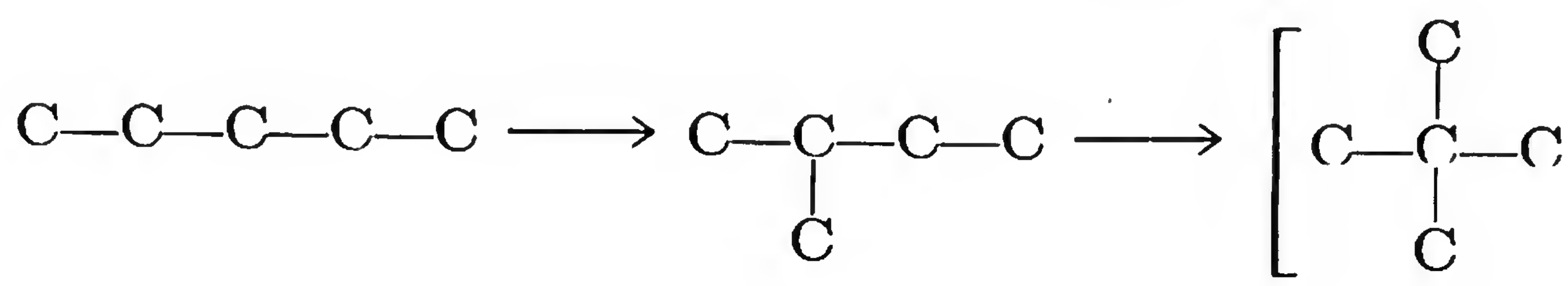
The catalyst may participate in an isomerization, either by activating the initial hydrocarbon or by forming an intermediate compound. Consequently, it seems logical to consider the types of union between the various isomers and the catalysts. Too great attraction of an isomer product for the catalyst may interfere with formation of the desired individual hydrocarbon. Preliminary investigations of effective catalysts for isomerization should include studies of their physical properties (degree of dispersion, surface activity, adsorption isotherms, lattice constants, electronic configuration) and chemical properties (valence, degree of unsaturation, degree of oxidation and reduction, acidity, alkalinity). A proper choice of catalyst may assist in the differentiation of intermediate stages of catalytic isomerization. Several examples in which acids and alkalies give cyclized and non-cyclized isomers, respectively, are considered in detail. Determinations of pH and pOH should prove valuable methods in the study of reaction reversibility involving acidity or alkalinity, respectively. Reversibility has been demonstrated also with metallic sodium and sodium ethylate (devoid of free sodium) as catalysts. When a non-specific catalyst, or two specific catalysts, accelerating reactions in opposite directions is present, the isomerization proceeds more or less reversibly, and a true equilibrium may be attained.

The isomerization rates may be regulated by adjusting the concentrations of the initial isomer, the catalyst, and the inhibitors (in the case of undesirable reactions). Short contact time should prove of value in confining the reaction to its intermediate phases. A temperature increase is synonymous with addition of energy, and an acceleration of endothermic reactions should follow its application. A proper choice of temperature may result in the formation of a desired isomer.

Application of very high pressures may aid in the formation of isomers with greater density than that of the initial hydrocarbon. For the production of symmetrical isomers, such as tetramethylmethane, pressure effects are probably of significance and should be investigated. In the few possible conversions of solid or liquid hydrocarbons into gaseous isomers, the use of a vacuum may be suggested.

Reversibility in isomerization, need for specific isomers, and possible

instability of resulting isomers introduces a selectivity factor. This factor is a function of all the reaction conditions susceptible of change. The applied sequence of reaction conditions is often of major importance. The conversion of a *n*-alkane into a highly branched isomer requires a sequence of structural changes. An appreciation of this fact may lead to the isolation of hitherto unisolated isomers, *e.g.*,



A sequence of isomerizations, such as isomer A ⟶ isomer B ⟶ isomer C, may be resolved or controlled by proper choice of catalyst and short contact time. As a general rule, the most symmetrical structural isomer or the next lower homolog (*e.g.*, 1,3,5- or 1,3-polyalkyl benzenes) and the most stable geometrical isomer (*trans*) will be formed preferentially.

Various types of side reactions are possible in the process of isomerization, due to general activation of the bonds within the molecule. The undesirable reactions include: alkylation, condensation, cracking, dealkylation, dehydrogenation, dehydrocyclization, aromatization, disproportionation, esterification, hydration, hydrogenation, oxidation, polymerization, and substitution. Side reactions in isomerization processes can be controlled by a proper choice of catalysts or by introduction of inhibitors counteracting the undesirable reactions.

Thermodynamics can be applied to isomerization of hydrocarbons since it indicates the possible (over-all) paths of isomer formation, and specifies the most favorable temperature and pressure conditions. Due to increasing movements of atoms and electrons as the temperature rises above absolute zero, no hydrocarbon can be considered perfectly stable. Furthermore, different bond strengths prevail in the molecule at the locations of C—H, C—C, C═C, or C≡C bonds. Resonance among several valence-bond structures modifies the bond energies of each type of linkage. The several bond effects are summed up or vested in a single quantity, H°_T, known as the heat of formation or "heat content" of the isomer. The importance of freedom of motion (translational, rotational, and vibrational) of the atoms comprising an isomer cannot be overlooked. This is appropriately expressed as TS°_T, which is the corresponding heat of atomic motions or the product of the entropy S°_T and the absolute temperature T. The two quantities, H°_T and TS°_T, are "opposing" potentials whose net or useful effect is known as the free energy, F°_T, of a substance. The course of any isomerization depends upon the difference, ΔF°_T, between the free energy of the final isomer and that of the initial

isomer. The free energy of isomerization, ΔF°_T, may be obtained by using any of the following formulas (involving the values of the two free energies or four corresponding "opposing" potentials):

$$\Delta F^\circ_T = \left(H^\circ_T - TS^\circ_T\right)_{\substack{\text{final}\\ \text{isomer}}} - \left(H^\circ_T - TS^\circ_T\right)_{\substack{\text{initial}\\ \text{isomer}}}$$

$$= \Delta H^\circ_T - T\,\Delta\,S^\circ_T$$

$$= \left(F^\circ_T\right)_{\substack{\text{final}\\ \text{isomer}}} - \left(F^\circ_T\right)_{\substack{\text{initial}\\ \text{isomer}}}$$

The equilibrium constant, which corresponds to a final steady state of isomerization, may be calculated from the thermodynamic quantities, using the following formulas:

$$\Delta\,H^\circ_T - T\,\Delta\,S^\circ_T = \Delta F^\circ_T$$

$$\Delta F^\circ_T = -RT \log_e K_{\text{equil.}}$$

$$\log_e K_{\text{equil.}} = -\frac{\Delta F^\circ_T}{RT} = -\frac{\Delta H^\circ_T}{RT} + \frac{\Delta S^\circ_T}{R}$$

$$\text{Antilog}_e\left(-\frac{\Delta H^\circ_T}{RT} + \frac{\Delta S^\circ_T}{R}\right) = K_{\text{equil.}}$$

$$K_{\text{equil.}} = \frac{\text{Fugacity of final isomer}}{\text{Fugacity of remaining initial isomer}}$$

where ΔH°_T = difference in heat content of isomers (the so-called "heat of isomerization" or the negative of the ordinary heat of reaction at constant pressure), in kilocalories (15°) per gram-mole. The calculation of ΔH°_T requires values of the heat of formation from carbon and hydrogen, or else the heat of combustion, for both initial isomer and final isomer. ΔH°_T is too small in value to be measured directly by ordinary calorimetry.

ΔS°_T = difference in entropy of isomers, in kilocalories (15°) per gram-mole per centigrade degree. Values of the entropy for both initial and final isomers are required. These can be measured directly by calorimetry or calculated by the methods of statistical mechanics.

ΔF°_T = difference in free energy of isomers, in kilocalories (15°) per gram-mole. ΔF°_T is obtained by subtracting $T\Delta S^\circ_T$ from ΔH°_T.

R = gas constant, in kilocalories (15°) per gram-mole per centigrade degree.

T = absolute temperature, in degrees Kelvin.

e = base of natural logarithms.

$K_{\text{equil.}}$ = equilibrium constant (approximately the ratio of partial pressures at moderate total pressure).

It is customary to report values of ΔH°_T, ΔF°_T, $T\Delta S^\circ_T$, ΔS°_T, and $K_{\text{equil.}}$ for various isomers at a standard reference temperature, 25°, and in terms of the 15° kilocaloric. The equilibrium constant is the ratio of the final isomer's fugacity to that of the remaining initial isomer. From its value several other ratios may be deduced approximately, involving the partial pressures, mole fractions, concentrations, weights,

or volumes, of the final isomer and remaining initial isomer. Thermodynamics, however, has no direct bearing upon the energy required for the activation of the initial isomer, the velocity of isomerization, or the selection of a suitable catalyst.

Isomerization is of theoretical and practical interest to both organic chemists and chemical physicists. Chemical and physical properties of isomers, the stability factor, and energy changes in isomerization have been of considerable concern to the chemical physicist. As a result, the concepts of chemical activity are becoming more precise. Investigations of stereochemical changes in molecules are concerned today with rotations of groups about the C—C bond, rather than with complete breaks in linkages or the related dissociation and reunion of groups. It is appropriate, therefore, to point out that the paths of isomerization are not all alike and that no single theory, or combination of theories, adequately covers the manner whereby the hydrocarbons isomerize. Although a vast amount of work has been carried out on isomers and their reactions, no well-grounded theories for alkane, cyclane, or alkyl benzene isomerizations are available. The experimental evidence in theories for alkene, alkadiene, alkyne, and cyclene isomerizations is better, because of the unsaturated or reactive character of these hydrocarbons. Since there is no general theory of isomerization, a specific theory is required for almost every type of change encountered in hydrocarbon isomerizations.

A careful examination of the many hypotheses and theories of related organic reactions has demonstrated that these are to be organized into classical and recent viewpoints. The classical points of view include the Lewis and Langmuir atom, the Baeyer strain theory, and postulated formations of addition compounds or of cyclized intermediate hydrocarbons. Only those explanations which adapt themselves readily and unequivocally are retained herein and applied to the various hydrocarbon isomerizations.

The more recent and still unconcluded mathematical viewpoints include electronic mechanics that are based principally upon wave mechanics, although quantum mechanics has its share as a related approach. On the basis of a changeable bonding for reactant and resultant, the concept of an activated complex with a mean life of 10^{-13} second is formulated. Such a molecule having a bonding approximately halfway between that of the reactant and resultant, with semi-valence or weakest bonds growing into main valence bonds and *vice versa,* cannot be readily represented. These modern viewpoints have been applied to isomerization in some cases. Their general application is prevented by the difficulty of the required methods. Electronic mechanisms may prove of importance in the future study of isomerization. The role of activated hydrocarbon molecules, intermediate activated complexes, resonance

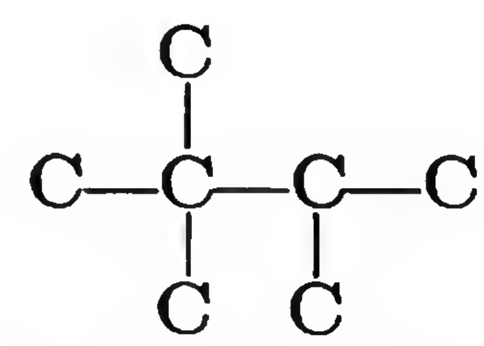
phenomena, and kinetics of isomerization should be studied in order to obtain a better understanding and a clearer insight into the isomerization process. The lack of analytical methods, and the increasing complexity and number of possible isomers in the case of higher members of the various hydrocarbon series make the subject of isomerization more complex.

Isomerization of hydrocarbons is bound to receive a wide practical application in the petroleum industry, similar to that of polymerization, aromatization, hydrogenation, dehydrogenation, and alkylation. The tendency toward that goal follows from (1) the recognition that isomerization, by a mere change in spatial configuration of carbon and hydrogen atoms, can produce selected hydrocarbons; (2) the significance which the production of selected hydrocarbons has in aviation and, therefore, in national defense; and (3) an appreciation of the fact that the antiknock property of motor fuels, expressed in terms of "octane number," is a function of molecular structure. It is generally recognized that chain branching in the alkanes and the orientation of their quaternary carbon atom toward the end of the molecule increase the octane number markedly, *e.g.*,

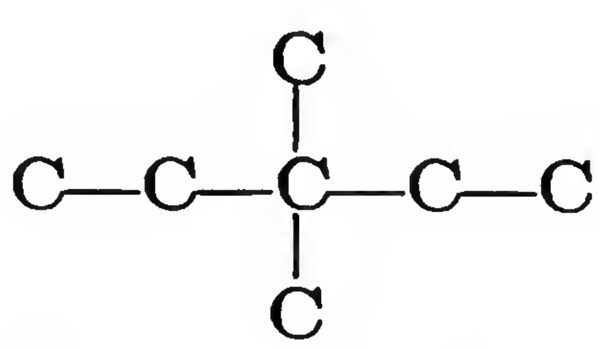
C—C—C—C—C—C—C

(0 Octane Number)

versus

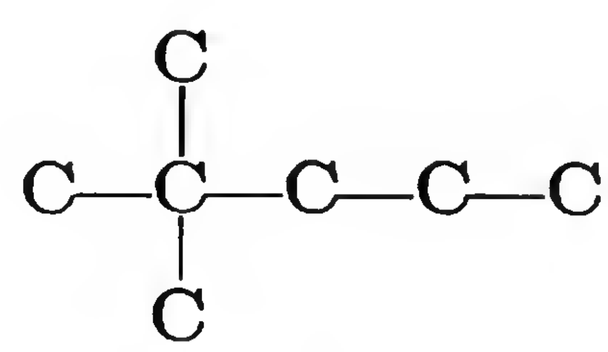


(101 Octane Number)



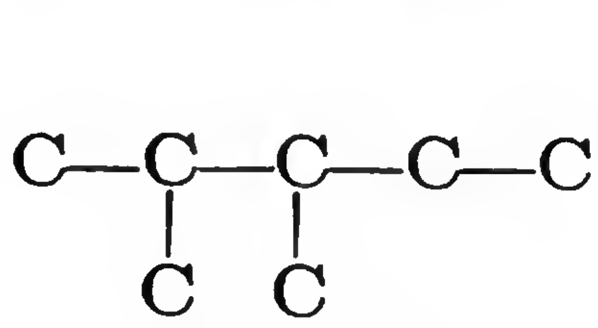
(84 Octane Number)

versus



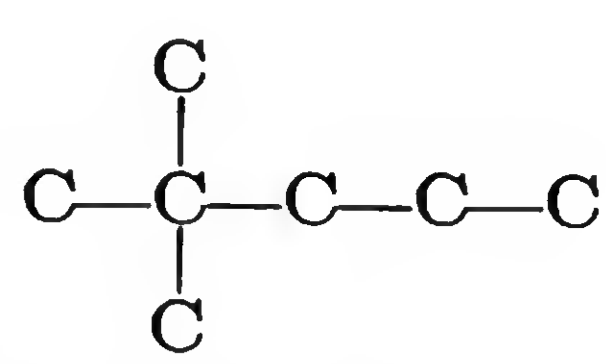
(93 Octane Number)

Likewise, movement of the side-chain toward the center in monomethyl alkanes increases the octane number. In the case of alkanes with one methyl group on each of two adjacent and centralized carbon atoms, the octane rating increases upon movement of the inner methyl group to the other carbon atom, *e.g.*,



(89 Octane Number)

versus



(93 Octane Number)

When the German air force tried to invade England in September, 1940, they were stopped by the R. A. F. who were using 100 octane gasoline in their motors, whereas Germany used 87. The 100 octane gasoline gave the English superior speed and maneuverability. The isomerization reaction played a role in the quality of the gasoline used.

100 Octane vs. 87 Octane Gasoline in Airplane Performance *

Aircraft	87 Octane	100 Octane
Max. speed at 2,750 rpm	236 mph	260 mph
Altitude for max. speed	15,700 ft.	17,300 ft.
Cruising at 60% max. power	192 mph	211 mph
at height of	15,700 ft.	17,300 ft.
Rate of climb at sea level	1,490 ft./min.	2,180 ft./min.
Rate of climb at 6,500 ft.	1,630 ft./min.	2,360 ft./min.
Rate of climb at 13,000 ft.	1,730 ft./min.	2,540 ft./min.
Rate of climb at 19,500 ft.	1,220 ft./min.	2,050 ft./min.
Time of climb to 6,500 ft.	4.2 min.	2.9 min.
Time of climb to 13,000 ft.	8.0 min.	5.6 min.
Time of climb to 19,500 ft.	12.3 min.	8.3 min.
Time of climb to 26,000 ft.	19.4 min.	12.2 min.
Service Ceiling	31,800 ft.	35,700 ft.
Absolute Ceiling	32,800 ft.	36,700 ft.
Engine		
Maximum output	830 hp	1,050 hp
Maximum power height	14,450 ft.	15,580 ft.

* The Institution of Automotive Engineers, Australia, *The Modern Engineer*, July 20, 1941.

Chapter I

Alkanes

This study discusses isomerization among all classes of hydrocarbons: alkanes, alkenes, alkynes, cyclanes, cyclenes, and aromatics.* It is appropriate that alkanes, the simplest class, be discussed first.

Methods Used in the Study of Isomerization

A perusal of the large number of possible structural and/or optical isomers among the alkanes (Tables 1, 2, and 3) will indicate that investigations of isomerization processes can be very complicated. A special difficulty exists in the lack of simple methods for the precise determination and identification of isomers, whose properties differ only slightly. The early methods were based upon inaccurate physical methods of separation, particularly fractional distillation of the isomerizate, followed by the comparison of a few physical constants for distillates and known isomers. At present, the separation and identification of isomers is greatly aided by recent developments in precision distillation,[83a, 94, 94a, 442b] molecular distillation,[636] and Raman spectra methods.[3a, 251, 317a, 473a] The methods of the Raman spectra, Sugden's parachor,[39a, 358a, 391a, 574c, 643a] Lorentz-Lorenz's molecular refraction,[97a, 162a, 355c, 355d, 575a, 643a] and related (additive) "structural functions," when used along with the usual analytical procedures, may be just as essential as tables of physical properties of hydrocarbons.†

Great difficulty is experienced in the analysis of alkane mixtures for individual isomers. The most practical methods in use consist of precise fractional distillation, followed by identification of fractions by their melting and boiling points, densities, and refractive indices. Raman spectra methods are capable of estimating the contents of 2 or 3 alkane isomers in admixture to within 5 per cent; mixtures of 4 or more alkanes are spectroscopically unresolvable. Practically no adequate chemical

* In the literature, isomerization of hydrocarbons has been discussed principally in conjunction with their catalytic and thermal reactions,[155] organic catalysis,[58a] thermal stability,[159] and thermodynamic properties.[17a, 428c, 442a, 475a, 477b, 651]

† The physical constants of all known alkanes, alkenes, alkynes, and other aliphatic hydrocarbons are collated and critically evaluated in the first volume of "Physical Constants of Hydrocarbons," by Egloff[151] (Reinhold Publishing Corp., 1939).

Table 1. Number of Isomeric Hydrocarbons of the Alkane Series (Excluding the additional isomers due to stereoisomerism)

From Henze and Blair[247]

Carbon Content	Number of Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
11	159
12	355
13	802
14	1,858
15	4,347
16	10,359
17	24,894
18	60,523
19	147,284
20	366,319
25	36,797,588
30	4,111,846,763
40	62,491,178,805,831

Note: The number of $C_{19}H_{40}$ isomers has been disputed by Perry.[435]

Table 2. The Number of Structurally Isomeric Alkanes. (Excluding the additional isomers due to stereoisomerism)

From Perry[435]

Carbon Content	Number of Isomers
19	148,284
21	910,726
22	2,278,658
23	5,731,580
24	14,490,245
26	93,839,412
27	240,215.803
28	617,105,614
29	1,590,372,121
31	10,660,307,791
32	27,711,252,769
33	72,214,088,660
34	188,626,236,139
35	493,782,952.902
36	1,295,297,588,128
37	3,404,490,780,161
38	8.964,747,474,595
39	23.647,478,933,969
60	22,158,734,535,770,411,074,184

Table 3. Number of Stereoisomeric and Non-Stereoisomeric Alkanes.

From Blair and Henze[67]

Carbon Content	Stereoisomers	Non-stereoisomers	Total
1	0	1	1
2	0	1	1
3	0	1	1
4	0	2	2
5	0	3	3
6	0	5	5
7	4	7	11
8	11	13	24
9	35	20	55
10	101	35	136
11	290	55	345
12	804	96	900
13	2,256	156	2,412
14	6.296	267	6,563
15	17,689	433	18,122
16	49,952	747	50,699
17	142.016	1,239	143,255
18	406.330	2,089	408,419
19	1.169,356	3,498	1,172,854
20	3.390.052	5,912	3,395,964

methods for the determination of isoalkanes are available. The Schaarschmidt or antimony pentachloride method[500] is a chemical procedure for the determination of "total isoalkanes" by means of a controlled chlorination. This method, including its modified and improved form (see Appendix I) suggested by Moldavsky and Livschitz,[381] is limited in its utility for the following reasons:

(1) It does not identify the individual isomers.

(2) Corrections must be made for a slower *n*-alkane chlorination that accompanies the main chlorination of isoalkanes.

(3) Tertiary carbon atoms of hexanes are chlorinated faster than those of octanes.

(4) Tertiary carbon atoms of octanes are chlorinated at unequal rates. 2,2,4-Trimethylpentane reacts incompletely or slowly.[39a]

(5) No information is given on the number of tertiary carbon atoms per molecule in a mixture of isomers.

(6) Quaternary carbon atoms are not chlorinated, and isomers containing them without tertiary carbon atoms in the same molecule cannot be distinguished from *n*-alkanes.

(7) Considerable disagreement[39a, 381, 436] exists regarding the extent of substitution of chlorine for hydrogen in given alkanes.

The foregoing limitations of the antimony pentachloride method serve to stress the need of a qualitative analysis of isomer products for struc-

ture, before their quantitative estimation. Bauer [39a] has investigated the utility of specific and molecular parachors for the determination of alkane isomers (for method see Appendix II). The parachors were found to be "additive functions" of the number of methyl groups in the molecule. A mixture of two isomers with different numbers of methyl groups in their molecules can be analyzed quantitatively by the method of parachors. However, the method is very limited in the absence of a qualitative analysis identifying the particular isomers present. For example, it cannot distinguish between a pure methylheptane, a mixture of *n*-octane and a dimethylhexane in equal quantities, or a mixture of *n*-octane and 2,2,4-trimethylpentane in 2:1 proportions.

Isomerization of Alkanes

Mechanism

The isomerization of alkanes, proceeding by change of carbon configuration, is accomplished by an *over-all* exchange of alkyl and hydrogen. It is an open question whether this exchange results from a direct process of rupture and recombination of the pertinent C—H and C—C bonds. The experimental evidence to date seems to favor direct rupture and recombination, due to the presence of products containing fewer and more carbon atoms than the starting material. The free radical theory of Frost, for thermal reactions in cracking, permits of an isomerization by a recombination of fragments.[198a] However, the observed formation of over 50 per cent of isomers in several catalytic isomerizations of alkanes cannot be overlooked, since such yields appear high for a statistical redistribution of fragments, including free radicals. The following communication [68a] discusses the plausibility of a free radical theory for alkane isomerization:

"Much more reasonable than this theory appears to be one which postulates that under the influence of a powerful catalyst the interatomic bonds of the alkane are loosened sufficiently to allow a rearrangement of the molecule as a whole to a thermodynamically more stable form by the slippage of atoms and groups of atoms *without their ever completely leaving the sphere of influence of the molecule as a whole.* Whether this bond-loosening (which may be expressed otherwise as a lowering of the activation energy of the molecule for isomerization) results from the formation of a definite hydrocarbon-catalyst complex or from the mere presence of the catalyst, through some electrical, magnetic, or dielectric influence, cannot at present be said.

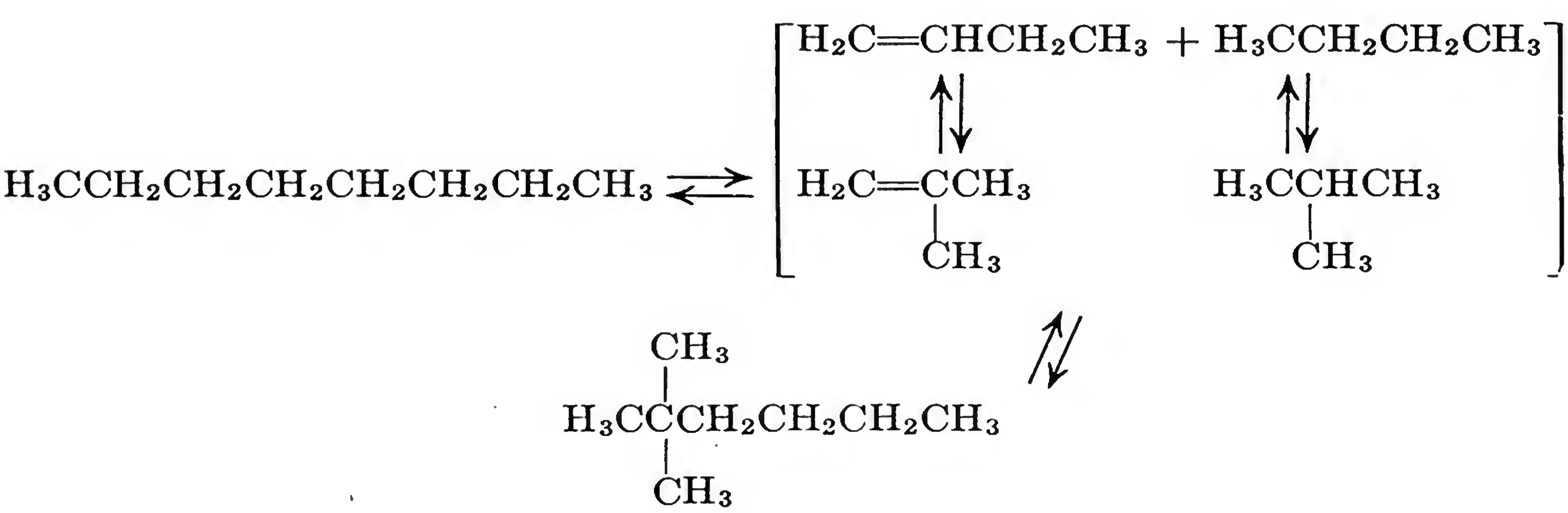
"If the bonds are sufficiently loosened, as by the use of too high a temperature with a given catalyst or too powerful a catalyst at a given temperature, atoms or groups of atoms may escape completely from the

molecular field of influence and rupture (cracking) occurs, with the formation of two or more atomic aggregates relatively independent of each other. If these should recombine, an isomer of the original hydrocarbon might be formed; it is more likely, however, that if they reacted further they would do so with other molecules or fragments, producing heavier and lighter molecules than the original. Under this theory, then, isomerization and cracking result from catalytic influences which are qualitatively similar but which differ in degree."

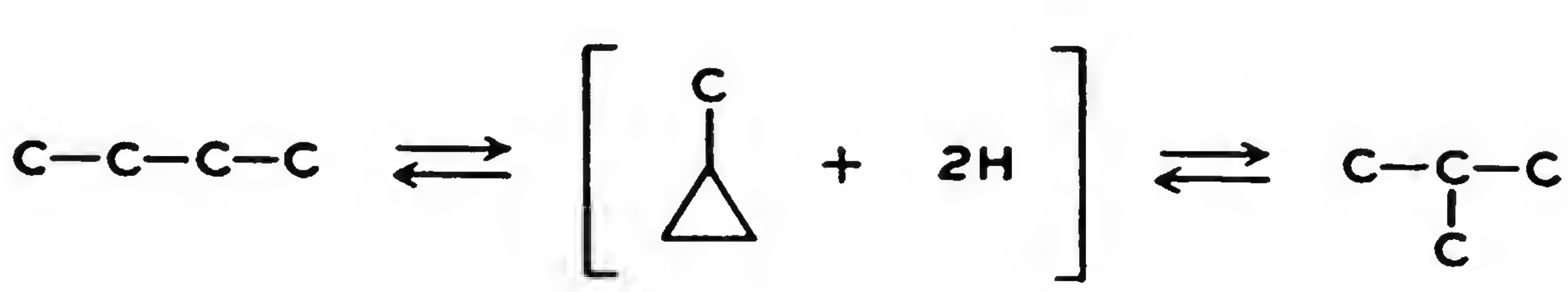
The actual mechanism of alkane isomerization may involve one or more of the following processes:

(1) *Dealkylation* of the alkane into an alkene and an alkane, by scission of hydrogen and the rupture of a C—C bond, followed by *recombination* in a new direction (through an alkylation of the lower alkane by the alkene, or by its corresponding ester if an "acid" catalyst is present):

$$CH_3CH_2CH_2CH_2CH_3 \rightleftarrows [CH_3CH{=}CH_2 + C_2H_6] \rightleftarrows CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$



(2) *Dehydrogenation + cyclization* and subsequent *decyclization + hydrogenation* at other points in the molecule:



This process is considered to be a mobile system of diyl forms that seldom, if ever, attains the illustrated, cyclic "intermediate" state of transformation.

(3) *Formation of radicals* (alkyl, alkenyl, and alkylidene) and their *recombination* in new directions:

$$CH_3CH_2CH_2CH_3 \rightleftharpoons CH_3CH_2\dot{C}H_2 + \dot{C}H_3$$

$$CH_3CH_2\dot{C}H_2 \rightleftharpoons \dot{C}H_2\dot{C}H_2 + \dot{C}H_3$$

$$\dot{C}H_2\dot{C}H_2 \rightleftharpoons CH_3CH<$$

$$CH_3CH< + \dot{C}H_3 \rightleftharpoons CH_3\dot{C}HCH_3$$

$$CH_3\dot{C}HCH_3 + \dot{C}H_3 \rightleftharpoons \begin{array}{c} CH_3CHCH_3 \\ | \\ CH_3 \end{array}$$

(4) *Isomerization unaccompanied by a hydrogen shifting,* as conceivable in the hexa-alkyl ethanes (R^1, R^2, R^3, R^4, R^5, R^6 representing combinations of alkyls):

$$\begin{array}{ccccc} & R^6 & & R^1 & \\ & | & & | & \\ R^5— & C & — & C & —R^2 \\ & | & & | & \\ & R^4 & & R^3 & \end{array} \quad \xrightarrow{\;?\;} \quad \begin{array}{ccccc} & R^1 & & R^6 & \\ & | & & | & \\ R^5— & C & — & C & —R^2 \\ & | & & | & \\ & R^4 & & R^3 & \end{array}$$

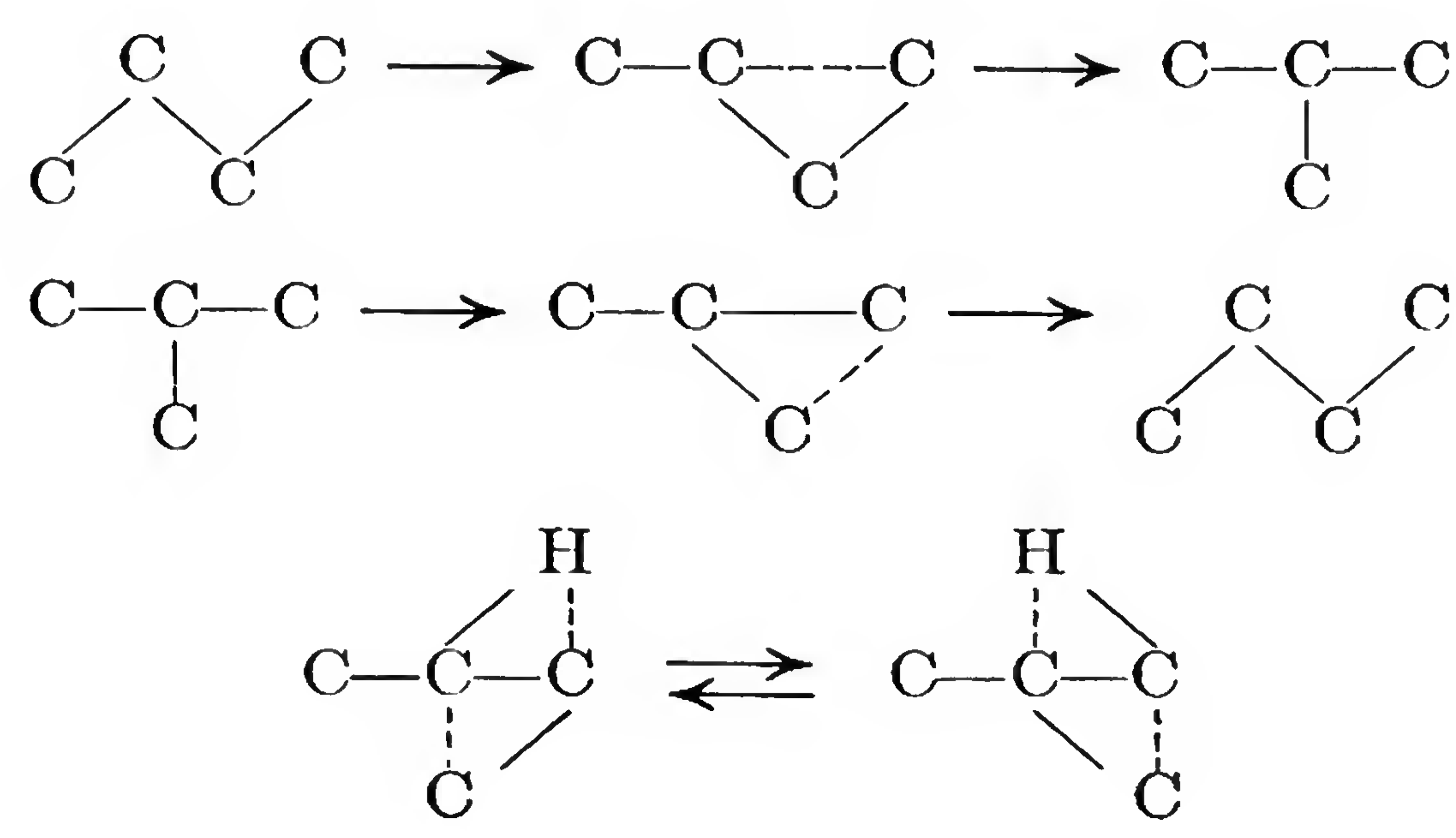
To date, none of these processes has been established in the isomerization of alkanes.* The direct alkylation of alkanes by alkenes in the presence of aluminum chloride,[278] boron fluoride,[277] or sulfuric acid,[5c] together with its simplicity, favors the first explanation (Process 1). The new alkane and alkene react, probably as radicals. Alkylation of alkanes by alkenes "without any catalyst" has been observed at elevated temperature (500-510°) and pressure (306 atmospheres).[193, 194, 424] It is of interest to consider at this point the basis of dealkylation plus alkylation leading to isomerization. With a catalyst, there may be a transfer of hydrogen and alkyl group *via* an intermediate. A general concept of the role of catalyst is an intermediate-compound formation between the hydrocarbon and the catalyst, as postulated for aluminum chloride reactions.[160] This should enable the reaction to proceed by a path requiring less activation energy than in the case of an uncatalyzed system, *e.g.*:

$$C—C—C—C + \text{cat.} \rightleftharpoons \begin{array}{c} C—C—C—C \\ | \\ H—\text{cat.} \end{array} \rightleftharpoons \begin{array}{c} H—C—C—C \\ | \\ C—\text{cat.} \end{array} \rightleftharpoons \begin{array}{c} C—C—C \\ | \\ C \end{array} + \text{cat.}$$

For thermal isomerization of alkanes *without a catalyst,* spatial possibilities may exist: "Compression-expansions" of the molecules and a

* There are many unsolved problems in the field of isomerization. Among these are the roles of activated hydrocarbon molecules,[15, 402, 411, 589] intermediate activated complexes,[131, 172, 173, 174, 210a, 260, 303a, 578a] and resonance[429, 430, 431, 432, 433, 543, 575aa, 640a] in isomerization.

"doubling-up" in space of the molecule due to collisions of molecules, whereby transfer of hydrogen and an alkyl group is favored. These physical interpretations adapt themselves readily for the explanation of isomerization in the case of either small or large alkane molecules. A small alkane may be used as an illustration:



The mechanism of thermal isomerization, on the other hand, may be conceived as a recombination of fragments of the decomposed molecule.[198a]

The dehydrogenation plus cyclization and subsequent decyclization plus hydrogenation (Process 2) is less favored as an explanation of alkane isomerization because it involves the migration of two hydrogen atoms. Moreover, cyclization to rings other than cyclopropanes and cyclobutanes as intermediates may give hydrocarbons of sufficient stability to resist the subsequent decyclization plus hydrogenation. Certain investigators consider substituted cyclopropanes as probable intermediates in isomerization.[219, 220] However, there are several objections to substituted cyclopropanes as intermediates in general molecular rearrangements.* [444, 634]

According to the free radical theory (Process 3), side reactions should accompany recombinations of radicals. Among free radical processes giving the same bivalent radical, it is uncertain whether dehydrogenation would precede dealkylation, or *vice versa*. Again, the postulated free radicals and reaction chains are an explanation which does not consider the role of the catalyst in isomerization. However, a catalyst may initiate the formation of a free radical, which starts the chain of reactions. The fact that the catalytic isomerization of *n*-butane yields propane, *n*-pentane, and isopentane as by-products fortifies the free radical theory

* Throughout this monograph, the word "isomerization" is used in preference to "intramolecular rearrangement" or "molecular rearrangement," because the last type of rearrangement generally requires a slight loss in final molecular composition and is usually an irreversible process, according to Porter.[13] Moreover, the term "molecular rearrangement of hydrocarbons" would be limited to movements of aliphatic, cyclic, or aromatic groups, thereby excluding many isomerizations involving a mere migration of hydrogen.

of alkane isomerization. The formation of a series of alkanes having increasing molecular weights may be the result of free radical processes occurring simultaneously or stepwise with the isomerization proper.

Changes in both C—H and C—C linkages are common to the first three processes. The recombination of fragments occurs by direct alkylation (Processes 1 and 4), hydrogenation (Process 2), or indirect alkylation (Process 3). Reversal of reaction directions in any of the first three processes should result in the formation of a *n*-alkane from its isomer, and *vice versa*. It can be stated that the isomerization of alkanes results from two over-all processes: dissociation in the presence of a catalyst, and recombination. The intermediate steps occurring in these two processes remain to be investigated completely.

Isomerizations

Thermal. There is a possibility in the numerous investigations carried out on thermal treatment of alkanes (especially at high temperatures) that isomerization takes place along with the usual cracking, dehydrogenation, and other reactions but has remained undetected because of analytical difficulties.[368] No alkane has been observed to isomerize under strictly thermal conditions in work prior to 1937.[155] * However, this does not mean that non-catalytic isomerization is impossible, but rather that the subject must be studied by varying the temperature, pressure, and time of contact.

A "thermal isomerization" of *n*-octane at 450-550° in a porcelain tube has been reported recently.[546a] The yield of isomeric octanes was poor, and further experimentation will be required to show that catalytic conditions were absent. The "subpyrogenic reactions" [197] of *n*-octane in a Durax glass tube at 280° to produce 2-methylheptane (?) may be considered a catalytic isomerization analogous to the established catalytic isomerization of cyclohexane in a special glass tube at 330°.[16] An optical type of alkane isomerization, such as that of *d*- or *l*-3-methylhexane, has not been studied to date. It should proceed thermally.

Aluminum Halides as Catalysts. Most of the experiments on the isomerization of alkanes have been carried out with the aid of aluminum chloride plus dry hydrogen chloride. The reaction is stated to proceed with considerable velocity at increased temperature after an induction period of about one hour (hydrogen chloride-forming) in the absence of added hydrogen chloride.[379] However, other work [276] indicates the neces-

* The thermal treatment of pure alkanes has been studied for butane at 365-1100°, isobutane (400-1100°), *n*-pentane (400-1071°), isopentane (400-1075°), tetramethylmethane (575°), *n*-hexane (425-1220°), isohexane (red heat), 2,3-dimethylbutane (575°), *n*-heptane (400-1093°), *n*-octane (280-800°), 2,5-dimethylhexane (489-576°), 2,2,3,3-tetramethylbutane (450-570°), 2,7-dimethyloctane (435-550°); tridecane, tetradecane, and pentadecane (elevated temperatures), and hexadecane (390-815°).

sity of having added hydrogen chloride present. Considerable evidence [160] is presented to the effect that the catalysis requires both an acid, $HAlCl_4$, and free aluminum chloride, although the arguments are concerned especially with the use of aluminum chloride as a catalyst for the Friedel-Crafts reaction. There is some evidence [232] that water or moisture can produce an active catalyst of the type $Al(OH)Cl_2$ corresponding to the alumina hydrate, $AlO(OH)$, proposed by Ipatieff as the active agent in isomerizations with alumina.[274] * Recently,[95] the formation of isobutane as the predominant gaseous product in aluminum chloride reactions [160] was ascribed to the rupture of the 2,3-bond in 2,2-dimethylated structures produced by isomerization of *n*-alkanes. The formation of isobutane was presented as evidence that isomerization precedes cracking (into simpler hydrocarbons), but there is no experimental evidence in support of this simple type of mechanism.

Butanes. A direct isomerization of *n*-butane into isobutane takes place at 175° and 35 atmospheres' pressure in the presence of *anhydrous* aluminum chloride and *dry* hydrogen chloride. This reaction proceeds with a 13 per cent isobutane formation during a 4-hour reaction time.[276] Recent patents [604, 605] disclose the conversion of butane into isobutane (66.5 per cent) by heating for 12 hours at 150° and 30 atmospheres' pressure in the presence of aluminum chloride (16.4 per cent) and hydrogen chloride (1.6 per cent). An increase in the concentrations of aluminum chloride and hydrogen chloride caused a drop to 13.3 per cent of isobutane, due to cracking reactions.[604] Another patent [165a] discloses examples wherein mixtures of aluminum chloride with partially dehydrated preparations of alumina, silica gel, pipe clay (kaolinite), pumice, or sodium permutite (an artificial zeolite) are catalysts at 100-150° for the isomerization of *n*-butane. The purpose of the partial dehydrations is apparently to control properly the formation of the requisite hydrogen chloride by a slow hydrolysis of aluminum chloride. A stable, granular catalyst, resistant to disintegrating influences at 200° and capable of converting *n*-butane into 53 per cent of isobutane, is prepared by mixing equal parts of anhydrous aluminum chloride and absorbent, or "activated," carbon. The catalyst is then transferred to a glass-lined pressure vessel, hydrogen chloride gas equal to 5 per cent by weight of the total mix is introduced, the pressure raised to 25 atmospheres with dry hydrogen, and the mixture heated at 250° for 3 hours with agitation.[284] More than 50 per cent of isobutane has been obtained in the liquid-phase reaction "within a few hours" from *n*-butane with anhydrous aluminum chloride at a temperature exceeding 70° and about 4 atmospheres' partial pressure of hydrogen chloride.[418, 420d, 422]

* Alumina is an important catalyst in organic chemistry operations. Its significance has been aptly pointed out.[282]

In other examples, both n- and isobutane were isomerized in the liquid phase at about 27° and 3 atmospheres' pressure in the presence of aluminum bromide (18.9 per cent).[384] The isomerizations proceeded rather slowly under these conditions, and over 2 months were required to attain the equilibrium state (78-82 per cent of isobutane and 18-22 per cent of n-butane), starting with either of the pure hydrocarbons. Traces of methane, ethane, and propane were formed as by-products. A study of the effect of aluminum bromide concentration on the rate of isomerization of n-butane at 30° indicated an approximately first-order dependence on the catalyst concentration under anhydrous conditions.[385] The rate constants were found to be between 0.030 and 0.044 mole per cent of isobutane per mole per cent of aluminum bromide per hour of treatment. Liquid-phase experiments giving a 15 per cent conversion of n-butane at 27° showed rate constants of 0.031-0.042 mole per cent of isobutane per mole per cent of aluminum bromide per hour in a glass vessel.[366] Stainless-steel vessels gave higher rates of isomerization.[366, 385] According to recent patents, n-butane can be isomerized in a liquid-phase reaction with 9.09 per cent by weight of aluminum bromide at 20° and 2.2 atmospheres' pressure to the extent of 1.3 per cent per hour. The converted hydrocarbon is drawn off at the top of a rectifying column attached to the reaction still, as gas containing 98-99 per cent of isobutane.[419, 422]

A series[382] of experiments concerning the equilibrium between n-butane and isobutane at 70-180° in the presence of aluminum chloride and added hydrogen chloride has furnished an equation showing the dependence of the equilibrium constant, K_p, on absolute temperature T:

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutane}}{n\text{-Butane}} = \frac{611}{T} - 1.204$$

According to this equation, the equilibrium concentrations of isobutane in the vapor state at atmospheric pressure should be 58, 63, 68, 71, and 79 per cent at 180°, 150°, 130°, 110°, and 70°, respectively. The observed equilibrium concentrations of isobutane, neglecting side reactions, amounted to 58, 63, 67, and 72 per cent at 180°, 150°, 130°, and 110°, respectively, under atmospheric pressure conditions, and to 74 per cent at 70° under the additional pressure required for a liquid phase. This equation can be compared with that corresponding to entropy values calculated for n-butane and isobutane by considering translational and rotational, but neglecting nuclear spin, contributions:[298]

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutane}}{n\text{-Butane}} = \frac{356}{T} - 0.8991$$

Other experiments indicate that the equilibrium concentration of isobutane in the vapor state at atmospheric pressure should be 64.5, 75.8,

but only 74.8 per cent at 140°, 100°, and 60°, respectively.[529a] The observed equilibrium concentrations of isobutane in the corresponding liquid phase, neglecting side reactions, were 64.5, 68.8, and 67.0 per cent at 140°, 100°, and 60°, respectively. One group of workers[135a] finds that the equilibrium constant, K_p, is 2.51 at 100°, corresponding to 71.5 per cent of isobutane after correcting for side reactions. The combined results of the several data[135a, 382, 384, 529a] on the n-butane-isobutane equilibrium, placed uniformly upon a vapor phase basis, can be readily shown to follow the equation:

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutane}}{n\text{-Butane}} = \frac{520}{T} - 1.000$$

The exothermic heat of isomerization of n-butane into isobutane at 25° has been calculated as 1.63 kilocalories,[475] 2.27 ± 0.20 kilocalories,[198] and recently as 2.20 ± 0.20 kilocalories[375] per gram-mole. One experimenter[366] has reported 2.10 ± 0.30 kilocalories per gram-mole for the temperature range 10-150°. This figure can be compared with 2.80 kilocalories per gram-mole for the temperature range 70-180°, which is an "average value" obtained from the experimental equilibrium equation[382] (*infra*) by multiplying 611 by $R \log_e 10$.

Pentanes. The isomerization of n-pentane into isopentane has been studied in both liquid and vapor phase with aluminum chloride plus promoters, and in the liquid phase with aluminum bromide alone.[216] No reaction was observed at atmospheric pressure when dry n-pentane was heated under reflux for several days with freshly sublimed aluminum chloride. Similarly, dry n-pentane in a vapor state, together with dry nitrogen, proved to be unreactive at 40-133° and atmospheric pressure when passed over freshly sublimed aluminum chloride. Addition of equivalent quantities of dry hydrogen bromide, dry hydrogen chloride, alkyl chlorides, hydrated aluminum chloride, or water, to aluminum chloride in the liquid-phase reaction resulted in the formation of butanes, isopentane (chief product), saturated higher-boiling products, and an insoluble unsaturated polymer. As in the work with butane,[276, 605] it was found that the reaction with aluminum chloride takes place only in the presence of hydrogen chloride, either added directly or generated immediately afterward from aluminum chloride by the addition of water. Typical proportions for the liquid-phase reaction were given as aluminum chloride (22.9-28.3 per cent) and water (0.6-0.8 per cent), or its equivalent. Substitution of aluminum bromide for aluminum chloride gave qualitatively the same products. Aluminum bromide, being more soluble in n-pentane, was taken as the more active catalyst; it catalyzed "without the addition of other substances." n-Pentane, reacting with anhydrous aluminum bromide (9.7 per cent) at room temperature and atmospheric

pressure, gave butanes (5.0 per cent, mostly isobutane), isopentane (55.9 per cent), compounds boiling higher than n-pentane (3.4 per cent), and insoluble tar (0.5 per cent). Vapor-phase reaction at 40° and atmospheric pressure, using promoter substances, caused a greatly increased formation of isobutane at the expense of isopentane. Higher-boiling substances and traces of hydrogen were formed also; the most active catalyst was found to be aluminum chloride and dry hydrogen bromide. Boron fluoride is also an effective activating agent for aluminum chloride.[37a]

Several recent patents [603, 605] disclose the conversion of a mixture of n-pentane and hydrogen chloride (1.0 per cent) to isopentane (27 per cent per pass, 80 per cent upon recycling) in a continuous process utilizing aluminum chloride on active carbon at 200° and 30 atmospheres' pressure. Another patent [420a] proposes the use of a complex compound of aluminum chloride and *tert*-butylbenzene, $C_{10}H_{14} \cdot 2AlCl_3$, as catalyst for isomerizations of n-pentane at 35° or 120°. Aluminum chloride catalysts, containing chlorosulfonic acid or fluorosulfonic acid, are stated to be of improved selectivity, *i.e.*, capable of preventing the formation of undesired alkenes or polymers by virtue of alkylating properties promoted by the halosulfonic acid.[357a]

A study has been made of various mixtures of n-pentane and isopentane in the presence of 2 mole per cent of aluminum bromide.[385] The results attained indicate an equilibrium concentration of isopentane near 90 per cent at 0° and between 70 and 100 per cent at 27°. Experiments on the same equilibrium, conducted in the liquid phase in the presence of aluminum chloride, hydrogen chloride, and hydrogen gas to suppress side reactions, show that the equilibrium concentration of isopentane decreases to 82 per cent at 80°.[529a] Other experiments [382a] indicate that the equilibrium concentration of isopentane in the liquid phase at 25°, 50°, 70°, and 90° is 86, 82, 78, and 74 per cent, respectively. These values have been recalculated to the vapor phase by means of Raoult's law, furnishing an equation showing the dependence of the equilibrium constant, K_p, on absolute temperature T:

$$\log_{10} K_p = \log_{10} \frac{\text{Isopentane}}{n\text{-Pentane}} = \frac{511}{T} - 0.820$$

Tetramethylmethane may be expected as a product of the isomerization of n-pentane or isopentane, but experimenters have not reported its presence. The unique molecular symmetry and relatively low density of tetramethylmethane warrant an investigation of the possible influence of various temperatures and absolute pressures, besides catalysts, upon isomerizations of the pentanes. An exothermic isomerization of n-pentane into tetramethylmethane at 25° and atmospheric pressure should occur with an energy release of 4.68 kilocalories per gram-mole.[312, 477] This

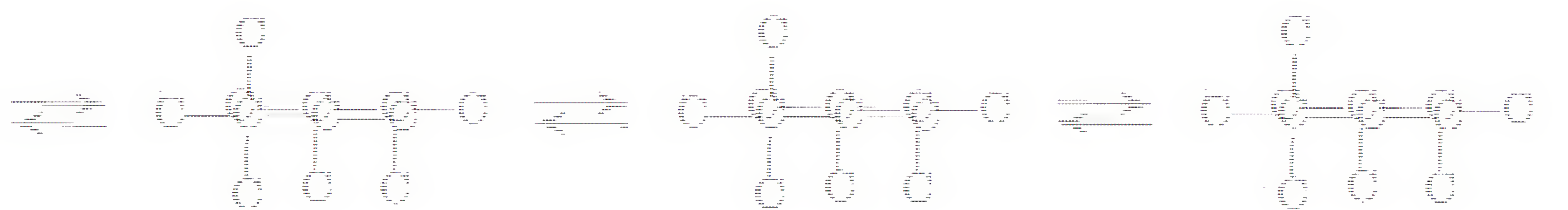
value (4.68 kilocalories) is more than double the heat of isomerization (1.63 kilocalories) of *n*-butane into isobutane.[475] This excess of energy over that for two C—C bonds may be due to stereochemical resistance in the introduction of the last methyl group. Tetramethylmethane proved to be completely stable at room temperature during 2300 hours of treatment with 5-10 mole per cent of aluminum bromide.[385]

Hexanes. *n*-Hexane, treated at its boiling point (68-69°) with aluminum chloride (27 per cent) and water (1.0 per cent) for 7.5 hours, gave a "considerable" amount of 2- and 3-methylpentanes, together with cyclohexane (1.45 per cent).[401] There is some doubt, however, about the resulting hydrocarbons, since the products were identified principally by their boiling points without using modern fractionation equipment. No reaction was noted when *n*-hexane was treated for 350 hours at 15-55° with aluminum chloride, unless propyl bromide was present.[520] *n*-Hexane gave 2- and 3-methylpentanes when acted upon by aluminum bromide at room temperature.[366]

The shaking[379] of *n*-hexane in a sealed glass tube with aluminum chloride (5 per cent) and some propyl chloride for 1-3 hours at 45-90° gave 23-28 per cent of isohexanes as determined by the antimony pentachloride method. It is claimed that propyl chloride serves only as a source of hydrogen chloride; this contradicts the viewpoint that propyl halides and aluminum chloride can be the source of a small amount of isohexanes via a Friedel-Crafts reaction.* Similar interpretations may be given for the results of experiments with propyl bromide addition.[379, 520]

n-Hexane, subjected to the action of aluminum chloride for 3 hours at 69-73° and atmospheric pressure in the presence of hydrogen chloride, gave isohexanes (55 per cent).[276] The isomers were isolated by fractionation and identified through their chemical properties and indices of refraction. Lower- and higher-boiling alkanes (20-25 per cent) accompanying the reaction contained isobutane (6 per cent) and pentane. The treatment of *n*-hexane in the liquid phase at 80° with aluminum chloride, hydrogen chloride, and hydrogen gas to suppress side reactions resulted in the formation of 48.4 per cent of methylpentane(s), 12.1 per cent of dimethylbutane(s), and 7 per cent of side products.[529a] It was concluded that the true equilibrium mixture for "hexanes" in the liquid phase at 80° should contain 75 per cent of methylpentanes, 20 per cent of dimethylbutanes, and only 5 per cent of *n*-hexane. *n*-Hexane yielded almost 44 per cent of isohexanes when autoclaved at 120° for about 2 hours with aluminum chloride.[39a] The content of isomers was

* The reactions $RCl + 2R'H \longrightarrow RH + R'R' + HCl$, and $RCl + R'H \longrightarrow RH + HCl + (R'$ minus H, *i.e.*, an alkene or cyclane) can be expected to result in $RCl + RH \longrightarrow RR + HCl$.



A study of the relative energy contents of the 5 hexanes indicates that isomerizations of liquid *n*-hexane at 25° and atmospheric pressure should release 1.335 ± 0.160, 0.754 ± 0.160, 3.446 ± 0.160, and 1.964 ± 0.160 kilocalories per gram-mole of 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, or 2,3-dimethylbutane, respectively, formed in the reaction.[477a] Another paper[453a] has submitted the following corresponding values: 1.30 ± 0.21, 0.76 ± 0.19, 3.49 ± 0.18, and 1.96 ± 0.20. The heat of isomerization of *n*-hexane into 2,2-dimethylbutane is approximately that of *n*-pentane into (theoretically) tetramethylmethane. The heat of isomerization of *n*-hexane into 2,3-dimethylbutane is roughly the sum of those of *n*-hexane into 2-methylpentane and into 3-methylpentane.

Heptanes. *n*-Heptane, heated under reflux for 24 hours with aluminum chloride (26.5 per cent) and water (1.0 per cent), gave a "large amount" of isoheptanes (11 per cent?).[401] Other products were hydrogen chloride, propane, isobutane, pentane and hexane fractions, high-boiling cyclanes, and unsaturated hydrocarbons. *n*-Heptane, treated in various portions with ethyl, propyl, isopropyl, and *n*-butyl chlorides in the presence of aluminum chloride at room temperature, gave less than 1.7 per cent of a possible dimethylpentane and less than 2.3 per cent of a possible methylhexane.[401] These experiments with alkyl halides are doubtful when considered from the isomerization viewpoint; the possibility of isomers being formed from lower hydrocarbons, by an alkylation via a Friedel-Crafts reaction, has not been settled to date.

Isomerization of *n*-heptane, together with the formation of higher- and lower-boiling hydrocarbons, occurred in the presence of aluminum chloride at temperatures of 96-98°.[96, 97] In one of the investigations,[96] a special technique was used, consisting of a continuous withdrawal of the low-boiling products from the reaction vessel, and several additions of a small portion of aluminum chloride to the system. The product consisted of a liquid boiling in a wide range, from which 3 hexanes and 5 isomeric heptanes were isolated by fractional distillation, as shown in Table 4.*

The treatment of *n*-heptane with aluminum chloride at 40° for 5 hours in the presence of sufficient anhydrous hydrogen chloride to initially saturate the mixture, yielded 13 per cent of isomers.[546a] Other products included 3.9 per cent of *n*-pentane plus *n*-hexane, 1.7 per cent of isopentane plus isohexanes, 2.7 per cent of higher *n*-alkanes, and 1.5 per cent of higher isoalkanes. The reaction of *n*-heptane containing 10 per

* In this survey an attempt has been made to put all experiments on a comparable basis by reporting the isomer yields in the form of per cent by weight on hydrocarbon introduced. Such measures as "cc. of product," "g. of product per cc. of charging stock," "per cent by volume," "mols per 100 mols reacted or decomposed," "mol per cent of catalyst in charging stock," and "drops or cc. of reactants" are but a step toward a quantitative formulation of "degree of isomerization."

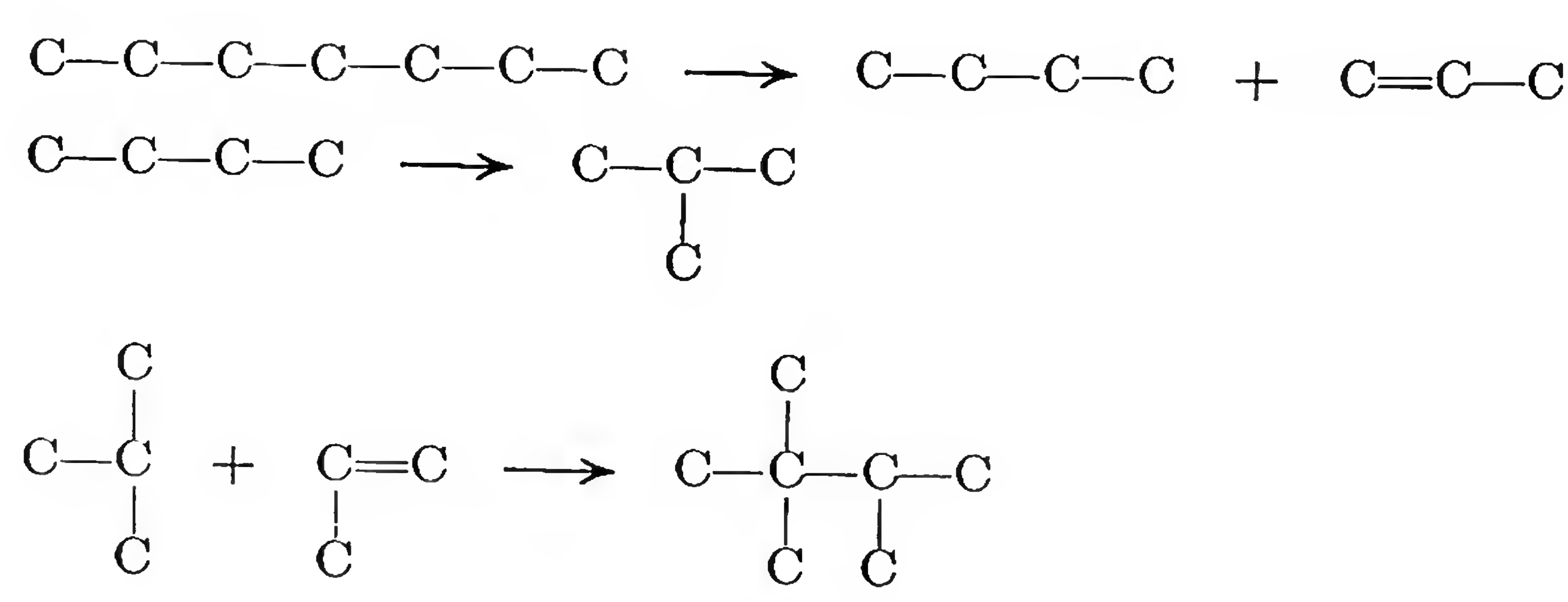
Table 4. Reaction of n-Heptane with Aluminum Chloride.[96]

Hydrocarbons Isolated	Weight per cent on n-Heptane Removed	Weight per cent on n-Heptane Introduced
Pentanes and lower alkanes	64.6	25.84
n-Hexane	0.4	0.16
2-Methylpentane	3.4	1.36
3-Methylpentane	2.0	0.80
n-Heptane	..	60.0
2-Methylhexane	1.2	0.48
3-Methylhexane	1.6	0.64
2,4-Dimethylpentane	1.5	0.60
3,3-Dimethylpentane	0.4	0.16
2,2,3-Trimethylbutane	0.5	0.20
Polymer products	24.4	9.76
	100.0	100.0

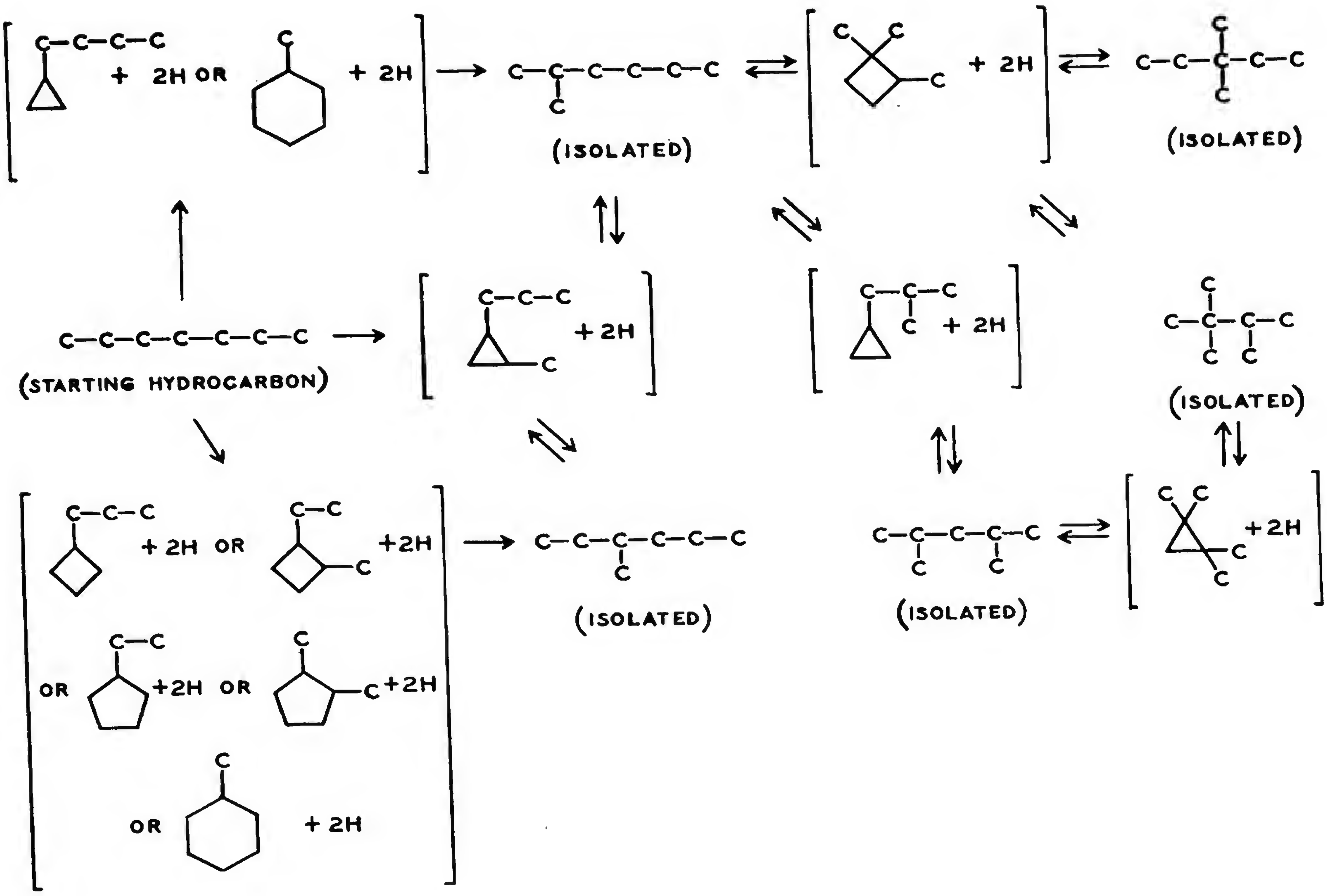
cent of its weight in aluminum chloride at 40-140°, for about 2 hours, led to the formation of 4.8-37.9 per cent of isoheptanes.[39a] The composition of the product was determined by the method of specific parachors.

n-Heptane, heated 3 hours at 220° and 50 atmospheres' initial pressure of hydrogen in the presence of aluminum chloride (1.0 per cent), gave isoheptanes (8 per cent).[437]

Since the various isomeric heptanes in the experiments[96] conducted at the "boiling point" were isolated and identified, it is interesting to analyze the possible mechanism and complexity of the reaction. For example, the formation of 2,2,3-trimethylbutane, the extreme case of isomerization, can be explained tentatively by a mechanism given by the alkylation theory:



According to this theory, propene is an important intermediate product and some should have been isolated. The polymer products may contain incorporated propene units, which would account for its absence. However, the formation of all isomers isolated in this isomerization of n-heptane, similar to that of n-hexane, may be explained also by the theory of dehydrogenation plus cyclization and subsequent decyclization plus hydrogenation. An interpretation of the foregoing isomerizations[96] in the heptane group follows:



Nevertheless, it is difficult to account for the presence of lower hydrocarbons by a theory stressing dehydrogenation rather than dealkylation.

In view of the quest for high octane-rating branched isomers among the alkane group of gasoline hydrocarbons (*i.e.*, hexanes, heptanes, octanes, and nonanes), it is evident that the alkylation and the cyclization plus decyclization theories have much to offer in investigations of the "routes" of isomerization. The octane rating scale is based on the volume per cent of 2,2,4-trimethylpentane ("isoöctane") in *n*-heptane mixtures. Pure 2,2,4-trimethylpentane, therefore, is rated as 100 and *n*-heptane as 0 in antiknock value. In this connection, it is interesting to present in Table 5 some of the octane ratings obtained by recent investigators.[561a] The effect of molecular structure upon the octane ratings of hydrocarbons is considered in a recent publication.[159a]

Octanes. *n*-Octane gave no isomers when treated with freshly-sublimed aluminum chloride for 24 hours at room temperature.[379] Saturation of the octane with hydrogen chloride effected an activation of the aluminum chloride (used 5 per cent for 22 hours and 10 per cent for 4 days) so that iso-structure octanes (24 and 61 per cent, respectively) were formed at room temperature. A 22-hour treatment of *n*-octane at room temperature with aluminum chloride (10 per cent) plus $PbSO_4 \cdot 2HCl$ or $CuSO_4 \cdot 2HCl$ (10 per cent, as sources of HCl) gave respectively 17.5 and 24.3 per cent of branched octanes. An analysis has

Table 5. Octane Numbers of Alkanes. [561a]

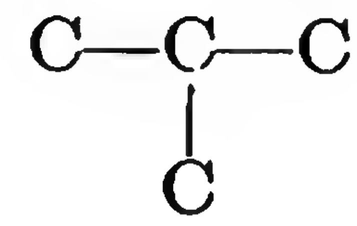
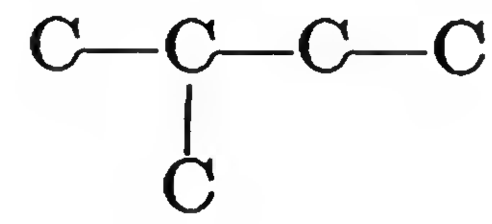
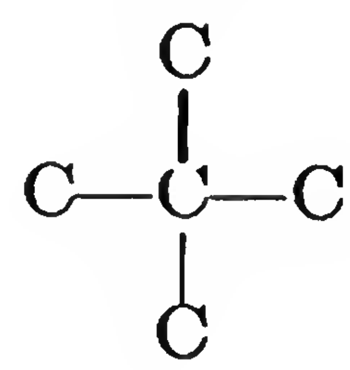
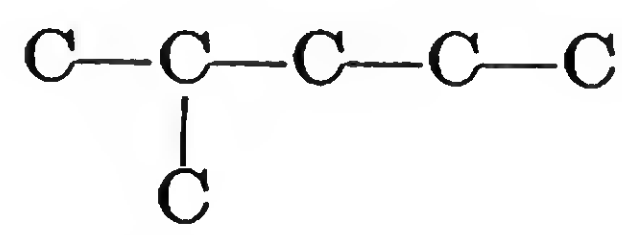
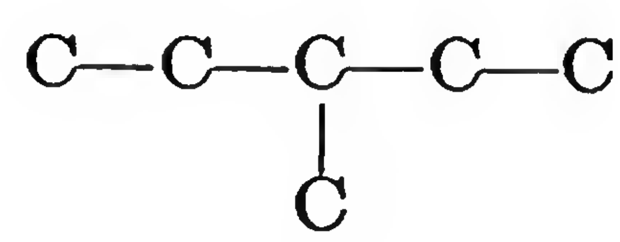
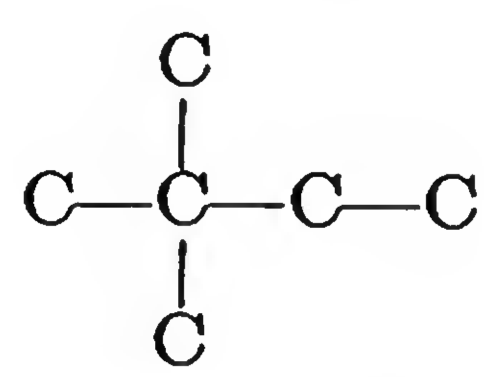
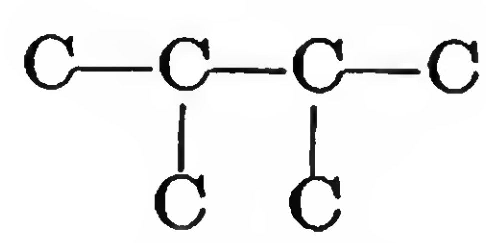
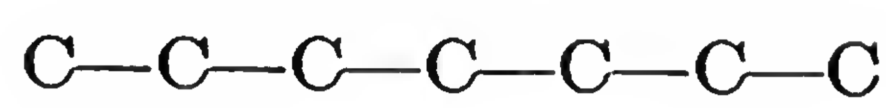
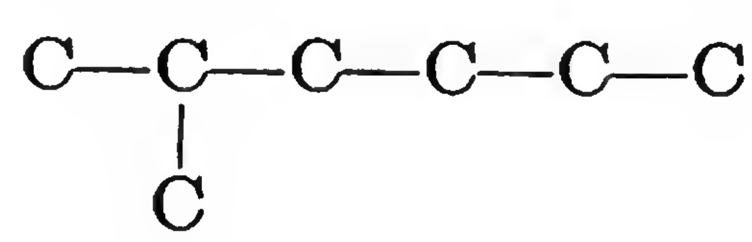
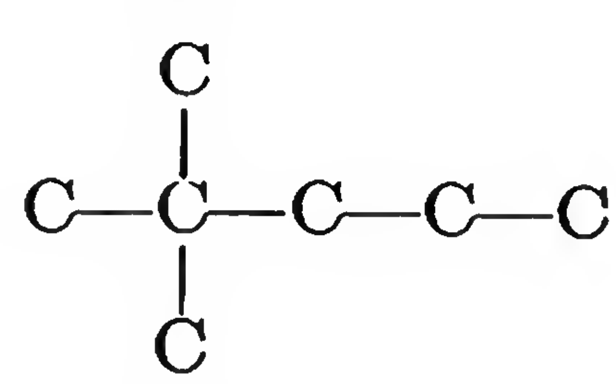
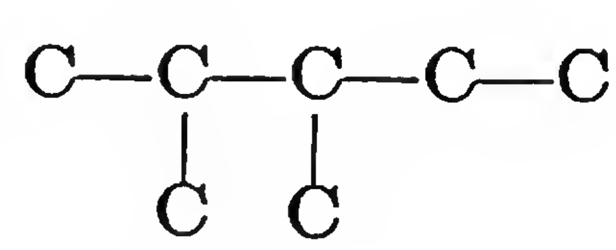
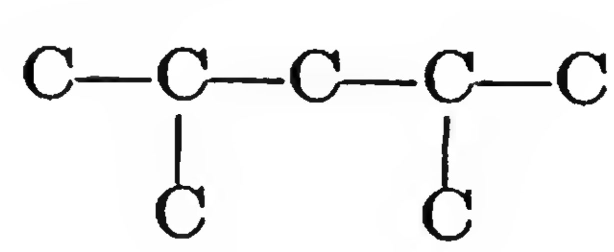
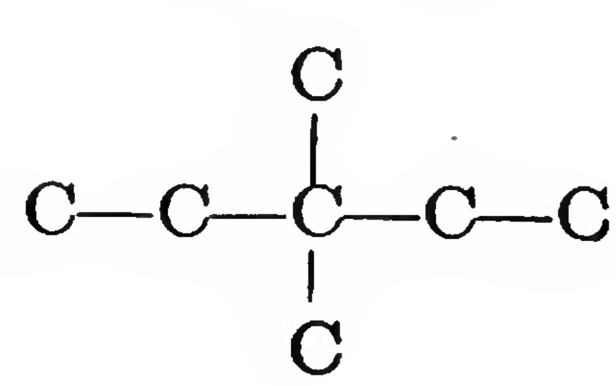
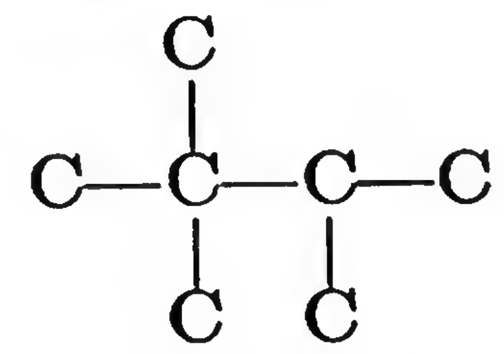
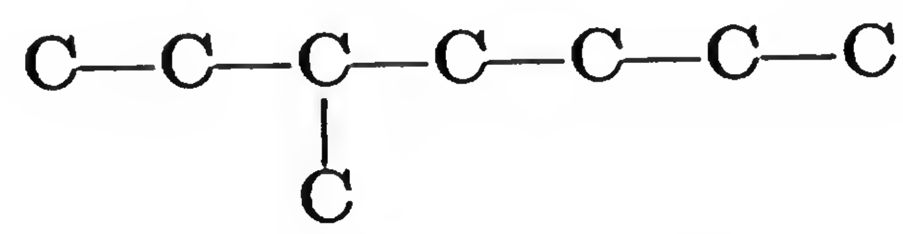
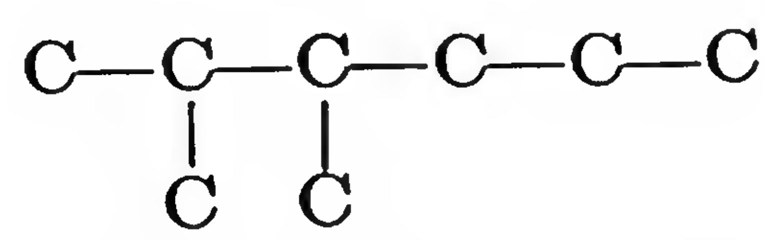
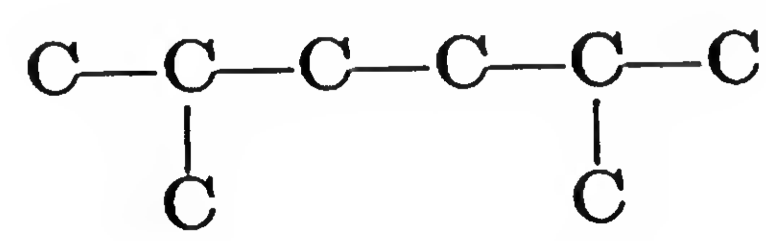
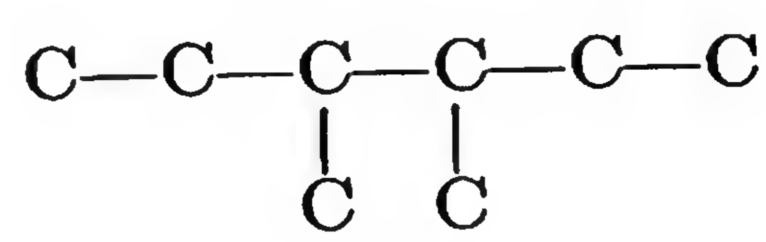
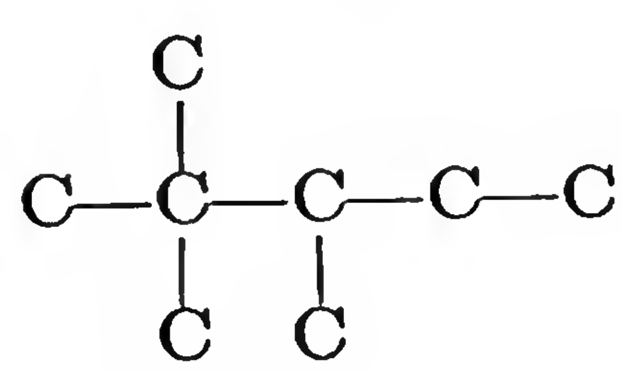
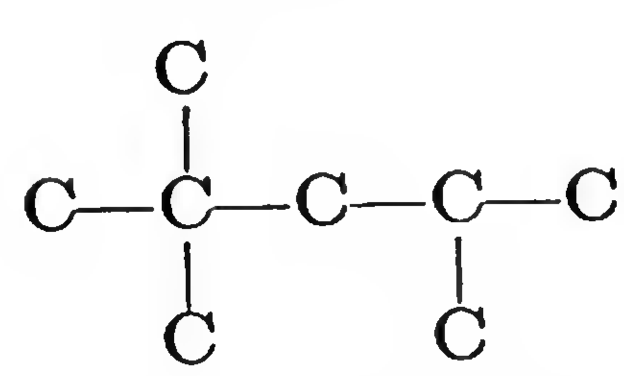
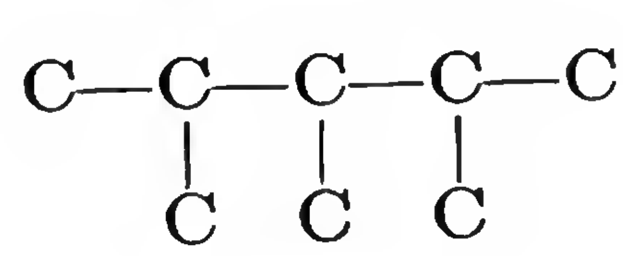
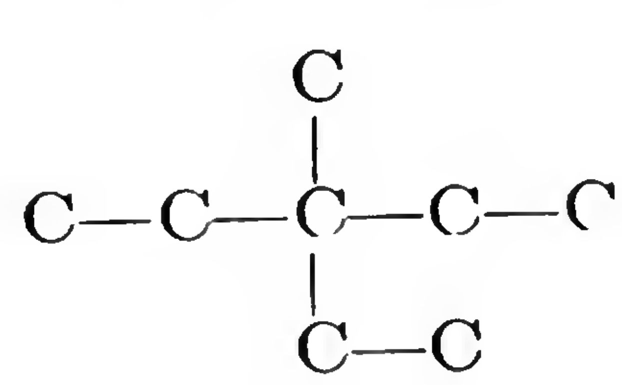
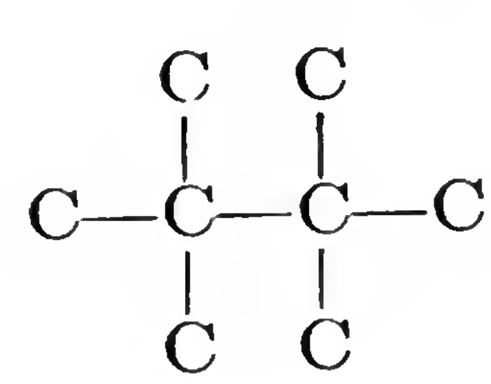
Alkanes		Octane Numbers (A. S. T. M.-C. F. R. Motor Method)
n-Butane		92
Isobutane		99
n-Pentane		61
Isopentane		89
Tetramethylmethane		83(?)
n-Hexane		25
2-Methylpentane		73
3-Methylpentane		75
2,2-Dimethylbutane		96
2,3-Dimethylbutane		95
n-Heptane		0
2-Methylhexane		45
2,2-Dimethylpentane		93
2,3-Dimethylpentane		89
2,4-Dimethylpentane		82
3,3-Dimethylpentane		84

Table 5.—*Continued.*

Alkanes		Octane Numbers (A. S. T. M.-C. F. R. Motor Method)
2,2,3-Trimethylbutane		101
n-Octane	C—C—C—C—C—C—C—C	−17
3-Methylheptane		35
2,3-Dimethylhexane		76
2,5-Dimethylhexane		52
3,4-Dimethylhexane		85
2,2,3-Trimethylpentane		102
2,2,4-Trimethylpentane		100
2,3,4-Trimethylpentane		97
3-Methyl-3-ethylpentane		91
2,2,3,3-Tetramethylbutane		103

been made of the products that result when *n*-octane is acted upon by aluminum chloride at 50-55° for 6 hours in the presence of sufficient anhydrous hydrogen chloride to initially saturate the mixture.[546a] The observed percentages of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, and higher *n*-alkanes were 0.65, 2.6, 2.1, 43.7, and 6.66, respectively, whereas those of isopentane, isohexanes, isoheptanes, *isoöctanes,* and higher iso-alkanes were 0.47, 1.9, 1.6, *17.2,* and 4.17, respectively. The depressed

quantities of *n*-heptane and isoheptanes are apparently indicative of a preferential scission of the octane chain between its second and third carbon atoms. *n*-Octane gave 4.7 and 12.8 per cent of isomers when subjected respectively to 20 per cent of aluminum bromide plus hydrogen bromide for 120 hours or to 20 per cent of aluminum chloride plus hydrogen chloride for 140 hours at room temperature.[374]

n-Octane, heated 3 hours at 405-410° with aluminum chloride (5 per cent) under 70 atmospheres' initial pressure of hydrogen, gave a product containing isoöctanes (23.3 per cent), together with lower- and higher-boiling hydrocarbons.[437] In an earlier work,[228, 571] no formation of isomers was observed from *n*-octane and from 2,5-dimethylhexane (*i.e.*, diisobutyl) under the action of aluminum chloride at 100-125°. The effect of temperature upon aluminum chloride-catalyzed isomerizations of *n*-octane can be readily seen from a series of "2-hour experiments" in which other variables were kept substantially fixed in value.[39a] The formation of isomers increased from 4.75 to 32.6 per cent as the temperature was varied from 40° to 140°.

2-Methylheptane and 2,2,4-trimethylpentane have been isomerized at 40-140° in the presence of 10 per cent by weight of aluminum chloride.[39a] The isomers developed during 2 hours at 140° attained a value of 16 and 15, respectively. These yields are considerably below those mentioned for *n*-octane. The content of isomers in each case was determined by the evaluation of specific parachors.

Other Catalysts. A number of catalysts have been found to isomerize alkanes, although their effectiveness varies considerably. For instance, the observation has been made[437] that *n*-octane under controlled conditions (3 hours at 410°, 70 atmospheres' initial pressure of hydrogen) gives increasing amounts of isomers in the following order of catalysts: zinc chloride, molybdenum trisulfide, and aluminum chloride.

n-Butane. The reaction of *n*-butane in the presence of molybdenum trioxide for 8 hours at 400° and 97 atmospheres' initial pressure of hydrogen gave only 5 per cent of isobutane, along with considerably more methane, ethane, propane, and unchanged *n*-butane.[283]

n-Pentane. Zirconium tetrachloride in the presence of hydrogen chloride at 150° effects an isomerization of *n*-pentane into 14 per cent of isopentane.[232a] A large quantity of isobutane, 41 per cent, is formed simultaneously.

Hexanes. The isomerization of *n*-hexane in sealed glass tubes for 6 hours at 420° was less than one per cent, without additions of catalysts, increasing to 1 and 3 per cent in the presence of molybdenum disulfide and silica, respectively.[380] Passage of *n*-hexane at atmospheric pressure through a copper spiral at 609° gave one per cent of isomers.[380] These isomerizations were considered as being secondary reactions, preceded

by cracking, but the arguments and evidence given are unconvincing. The isomers were identified by means of antimony pentachloride. *n*-Hexane, heated 2 hours at 400° and 90 atmospheres' initial pressure of hydrogen in a steel autoclave with 20 per cent of molybdenum disulfide, gave 27 per cent of isomers as determined by nitration.[408]

The agitation of 2-methylpentane for 500 hours with 96-per cent sulfuric acid gave a mixture containing 64.7 per cent of 2-methylpentane and 35.3 per cent of 3-methylpentane.[366] An identical treatment of 3-methylpentane yielded a similar mixture with 62.5 and 37.5 per cent of 2-methylpentane and 3-methylpentane, respectively.

Heptanes. *n*-Heptane, heated 6 hours at 300° and 50 atmospheres' initial hydrogen-pressure in the presence of zinc chloride (5 per cent), gave 27 per cent of isomers as determined by antimony pentachloride, but the yield was reduced to 18 per cent of isomers in a 7 hours' treatment at 400° and 60 atmospheres' pressure of hydrogen.[437] Fifteen per cent of isomers (by the antimony pentachloride method) were formed when *n*-heptane was heated 7 hours at 400° and 60 atmospheres' initial nitrogen-pressure in the presence of molybdenum trisulfide (5 per cent) plus cupric oxide (5 per cent).[437] The other products of these reactions had a wide distillation range. *n*-Heptane was heated 2 hours at 400° with 9.0 per cent of molybdenum disulfide under 140 atmospheres' pressure of hydrogen, giving 11 per cent of isomers as determined by nitration and subsequent reduction.[407]

Heating of *n*-heptane (not pure) with molybdenum trisulfide (5 per cent) at 420° and 70 atmospheres' initial hydrogen pressure showed that isomerization increases with reaction time as follows: 11 per cent of isomers in 3 hours, 19 per cent in 7 hours, and 20 per cent in 14 hours.[437]

2,4-Dimethylpentane yielded about 15 per cent of 2,3-dimethylpentane when stirred with 97-per cent sulfuric acid for 2 hours at 50°.[95c] This isomerization is an interesting one, because similar primary or secondary isomerizations occur in the alkylation of isoalkanes by alkenes in the presence of sulfuric acid.[65b, 65c] Intermediary formation of methyl hydrogen sulfate or dimethyl sulfate would partly explain these isomerizations.

n-Octane. *n*-Octane, heated 24 hours at 280° in a Durax-glass bomb tube, gave a 98-per cent yield of mixed octanes.[197] The isomerization was termed a "subpyrogenic reaction," but the product was not investigated thoroughly. An examination of the boiling points and densities of individual fractions comprising the mixed octanes, by reference to critically evaluated physical constants,[152] indicates a mixture of *n*-octane with 2-methylheptane. There is some indication that the addition of sulfur to the *n*-octane under comparable conditions leads

momentarily to 2,3,4-trimethylpentane, since thiophthenic derivatives were isolated.[197] The last hydrocarbon was not isolated.

n-Octane remained unisomerized when passed through a copper spiral at 591° and atmospheric pressure or when heated 2 hours at 325° in a small silver-lined steel pressure apparatus.[380] Pressure treatment of *n*-octane with the silver-lined steel apparatus at 450° gave 6 and 9 per cent of isomers in 2 and 3.7 hours, respectively.[380] Removal of the silver lining resulted in 11 per cent of isomers at 450°, whereas use of a large steel autoclave at 475° gave 10 per cent.[380] These "isomerizations" were considered to be the result of secondary reactions among products from a preliminary cracking.

n-Octane, heated 3 hours at 410° under 70 atmospheres' initial hydrogen-pressure in the presence of zinc chloride (5 per cent), gave 11.7 per cent of isomers (by the antimony pentachloride method).[437] Heating of *n*-octane for 3 hours under 70 atmospheres' initial hydrogen pressure in the presence of molybdenum trisulfide (5 per cent) gave no change at all at 360°, but formed 18 and 23.6 per cent of isomers (determined by the antimony pentachloride method) at 410° and 440°, respectively.[437] Unsaturated and aromatic hydrocarbons totaled 8 per cent at 440°, indicating that considerable cracking occurs at the point of maximum isomerization. All these reactions gave products with a wide distillation range.

It has been found that isomerization of *n*-octane takes place in the presence of certain dehydrogenation catalysts at 300-310° and atmospheric pressure.[659] Catalysis with nickel-alumina, and platinum on activated carbon, resulted in the formation of 5.5 and 15 per cent of isomers, respectively. Nickel on zinc oxide was tested also, giving 6.4 per cent of isomers. The first two experiments are particularly interesting, since no unsaturates were found in the reaction products. Alumina or activated carbon alone produced 4 per cent of isomers from *n*-octane at 310°.[659] The isomers were determined by the antimony pentachloride method. *n*-Octane, passed over alumina at 300-310° under atmospheric pressure, gave 10-12 per cent of isomers as determined by the antimony pentachloride method.[318]

n-Decane. *n*-Decane in the presence of nickel-alumina at 350° formed 1.6 per cent of isomers (determined by the antimony pentachloride method), together with 6 per cent of aromatics whose formation was due to a dehydrogenation plus cyclization.[319]

It must be noticed that the isomerization of *n*-octane and *n*-decane in the presence of a *dehydrogenating* catalyst terminates without formation of unsaturates other than those of aromatics; the product has a very narrow boiling range and seems to consist of unchanged alkane, isoalkanes, and aromatics. This fact must not be overlooked; it implies

that higher alkane isomerization may occur by dehydrogenation to an alkane, followed by isomerization to an isoalkene, and this succeeded by a disproportionation to an isomeric alkane and an aromatic. Numerous examples are known wherein unsaturated hydrocarbons undergo an irreversible disproportionation into more-saturated and less-saturated hydrocarbons in the presence of dehydrogenating catalysts.[70, 71, 95b, 121, 125, 150, 218, 221, 303b, 336a, 340, 341, 342, 344, 346, 347, 348, 350b, 350c, 358b, 358c, 359, 361, 428b, 467, 480a, 540a, 540b, 594a, 645a, 663a, 663b, 664, 665, 669a, 671a, 671b]

The past few years have seen a large advancement in thermodynamic data applicable to isomerization of hydrocarbons. It is appropriate, therefore, to submit a summary of the work that has been done on the alkanes to date. A recent paper[477b] has reported values of comparative thermodynamic quantities for the butanes, pentanes, hexanes, and heptanes, all in the ideal gaseous state, at temperatures ranging from 25° to 727°; these values are reproduced in Table 5a.

From these data, Figures 1-10 were plotted[477b] as a function of the absolute temperature. Figures 1-4 show which of the isomers is thermodynamically the most stable $\left(\text{lowest value of } \frac{\Delta F^\circ_T}{T}\right)$, which is the least stable $\left(\text{highest value of } \frac{\Delta F^\circ_T}{T}\right)$, and give the stability order of the intermediate isomers. The ordinate designation, $\Delta F^\circ/T$ in cal/(deg mole), corresponds to this monograph's $\frac{\Delta F^\circ_T}{T}$ in gram-calories per gram-mole per degree Kelvin. Figures 5-8 show how one mole of alkane molecules distribute themselves among the various isomeric forms at thermodynamic equilibrium in the gaseous state from 260 to 1060° K., for those pressures where the ratio of fugacity to pressure is substantially the same for the given isomers. The vertical width of a band at a given temperature measures the equilibrium mole fraction of the indicated isomer present in the gas phase. Figures 9-10 compare the available data on the direct determinations of the equilibrium concentrations of *n*-butane and isobutane, as well as *n*-pentane and isopentane, with the values for the same quantities (solid line) derived from the summarized data (*infra*).

From the foregoing data, the following statements were drawn with regard to the isomerization of butanes, pentanes, hexanes, and heptanes in the gaseous state:[477b]

"(a) At 25° C., the normal isomer is thermodynamically the least stable in each case, with the exception that 3-ethylpentane is less stable than *n*-heptane.

"(b) Relative to the other isomers, the normal isomer increases in

(Text cont'd on p. 50)

Table 5a. Summary of Values of the Thermodynamic Function $\Delta F^\circ_T/T$ in gram-calories per gram-mole per degree Kelvin, the Corresponding Equilibrium Constants K = Fugacity of Isomer/Fugacity of n-Alkane, and the Corresponding Equilibrium Concentrations N in Mole Fraction of the Total Isomerizate, for the Isomerization of the Butanes, Pentanes, Hexanes, and Heptanes in the Ideal Gaseous State, from 298° to 1000°K. (Rossini, Prosen, and Pitzer)

Temperature		Butanes						Pentanes								
		n-Butane			Isobutane			n-Pentane			2-Methylbutane			2,2-Dimethylpropane		
t°C.	T°K.	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N
25	298	0	1	0.28	−1.86	2.55	0.72	0	1	0.03	−5.28	14.3	0.44	−5.65	17.1	0.53
127	400	0	1	0.44	−0.47	1.27	0.56	0	1	0.11	−3.64	6.23	0.65	−1.65	2.30	0.24
227	500	0	1	0.54	0.35	0.84	0.46	0	1	0.18	−2.68	3.86	0.69	0.59	0.74	0.13
327	600	0	1	0.60	0.83	0.66	0.40	0	1	0.24	−2.11	2.89	0.67	1.98	0.37	0.087
527	800	0	1	0.68	1.44	0.48	0.32	0	1	0.32	−1.38	2.00	0.63	3.75	0.15	0.048
727	1000	0	1	0.72	1.86	0.39	0.28	0	1	0.37	−0.92	1.59	0.59	4.78	0.09	0.034

Temperature		Hexanes														
		n-Hexane			2-Methylpentane			3-Methylpentane			2,2-Dimethylbutane			2,3-Dimethylbutane		
t°C.	T°K.	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N
25	298	0	1	0.013	−3.33	5.34	0.071	−1.25	1.88	0.025	−8.22	62.6	0.84	−2.78	4.05	0.054
127	400	0	1	0.061	−1.98	2.71	0.16	−0.43	1.24	0.075	−4.58	10.0	0.61	−0.81	1.51	0.092
227	500	0	1	0.13	−1.25	1.88	0.24	0.09	0.96	0.12	−2.37	3.30	0.41	0.35	0.84	0.105
327	600	0	1	0.19	−0.74	1.45	0.27	0.39	0.82	0.15	−0.91	1.58	0.29	1.14	0.56	0.104
527	800	0	1	0.26	−0.15	1.08	0.28	0.72	0.70	0.18	0.75	0.69	0.18	1.99	0.37	0.096
727	1000	0	1	0.31	0.24	0.89	0.27	0.86	0.65	0.20	1.68	0.43	0.13	2.49	0.29	0.088

Temperature		Heptanes																										
		n-Heptane			2-Methylhexane			3-Methylhexane (racemic mixture)			3-Ethylpentane			2,2-Dimethylpentane			2,3-Dimethylpentane (racemic mixture)			2,4-Dimethylpentane			3,3-Dimethyl pentane			2,2,3-Trimethylbutane		
t°C.	T°K.	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N	$\Delta F^\circ_T/T$	K	N
25	298	0	1	0.009	−4.01	7.52	0.068	−3.62	6.18	0.056	1.43	0.49	0.004	−6.99	33.7	0.30	−6.75	29.9	0.27	−4.57	9.98	0.090	−4.80	11.2	0.100	−4.85	11.5	0.103
127	400	0	1	0.032	−2.59	3.68	0.12	−2.69	3.87	0.13	1.81	0.40	0.013	−3.09	4.73	0.15	−4.49	9.57	0.31	−1.79	2.46	0.079	−2.29	3.16	0.102	−1.47	2.09	0.068
227	500	0	1	0.062	−1.74	2.40	0.15	−2.14	2.94	0.18	2.22	0.33	0.020	−0.84	1.53	0.10	−3.08	4.71	0.29	−0.18	1.09	0.068	−0.62	1.37	0.085	0.60	0.74	0.046
327	600	0	1	0.092	−1.13	1.77	0.16	−1.70	2.36	0.22	2.47	0.29	0.027	0.60	0.74	0.068	−2.10	2.88	0.27	1.00	0.60	0.056	0.44	0.80	0.074	1.92	0.38	0.035
527	800	0	1	0.14	−0.42	1.24	0.17	−1.22	1.85	0.26	2.78	0.25	0.035	2.33	0.31	0.044	−0.87	1.55	0.22	2.38	0.30	0.043	1.68	0.43	0.061	3.49	0.17	0.024
727	1000	0	1	0.17	−0.12	1.06	0.18	−1.02	1.67	0.29	2.96	0.23	0.03[illegible]	3.28	0.19	0.033	−0.14	1.07	0.18	3.06	0.21	0.037	2.34	0.31	0.053	4.35	0.11	0.019

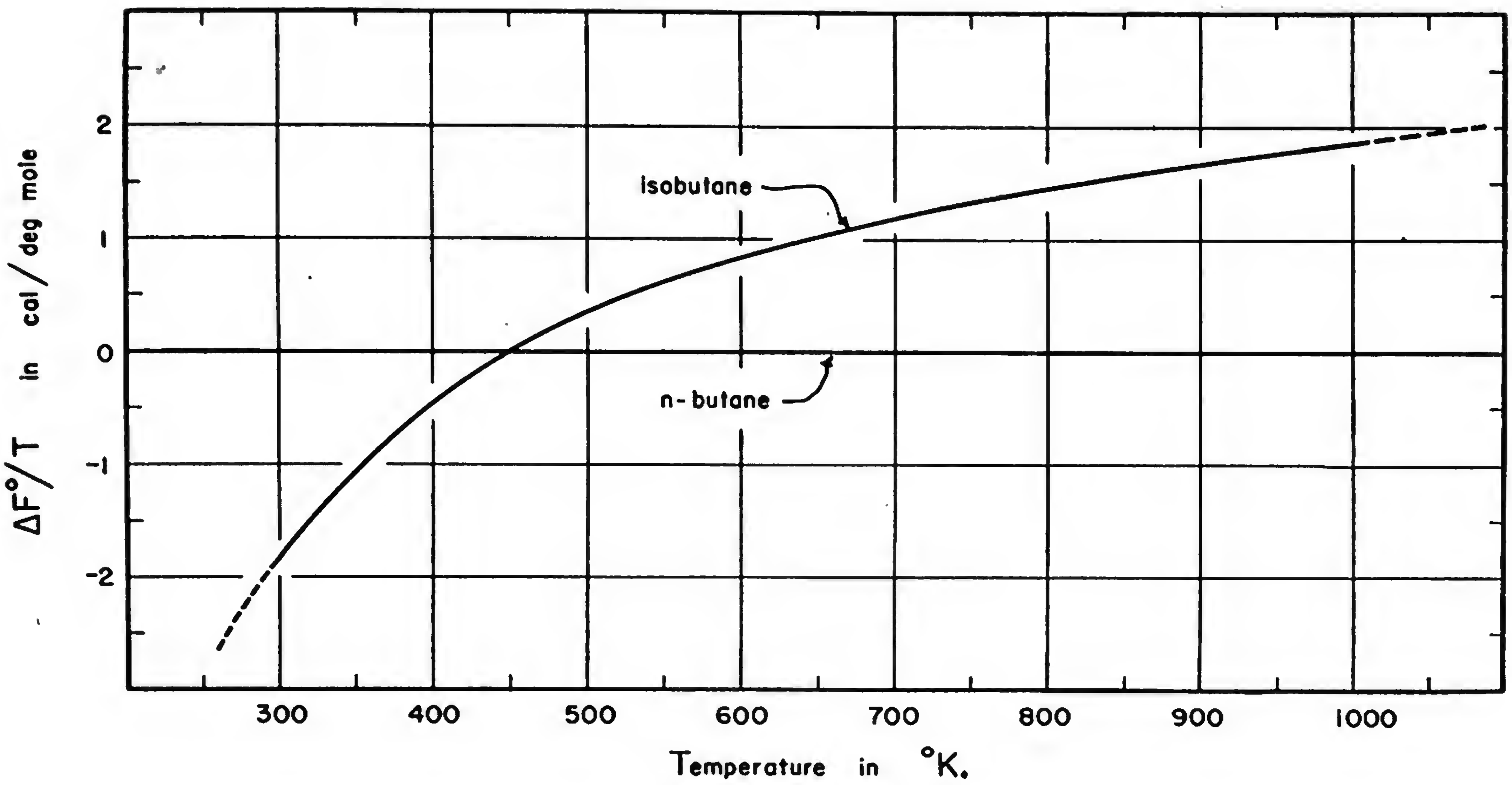

ΔF°/T in cal/deg mole
2
1
0
-1
-2
300
400
500
600
700
800
900
1000
Temperature in °K.
isobutane
n-butane

FIG. 1.

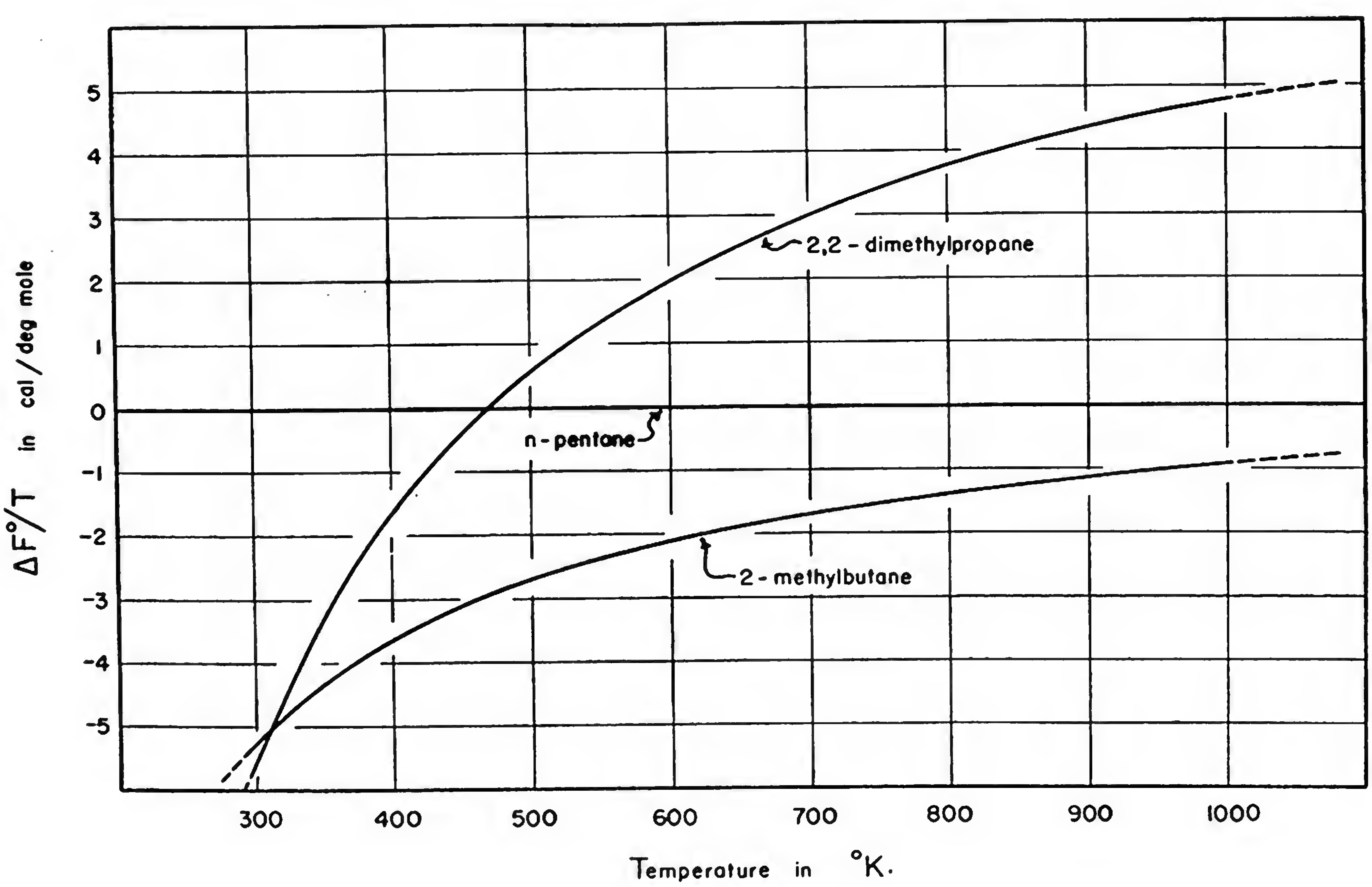

ΔF°/T in cal/deg mole
5
4
3
2
1
0
-1
-2
-3
-4
-5
300
400
500
600
700
800
900
1000
Temperature in °K.
2,2-dimethylpropane
n-pentane
2-methylbutane

FIG. 2.

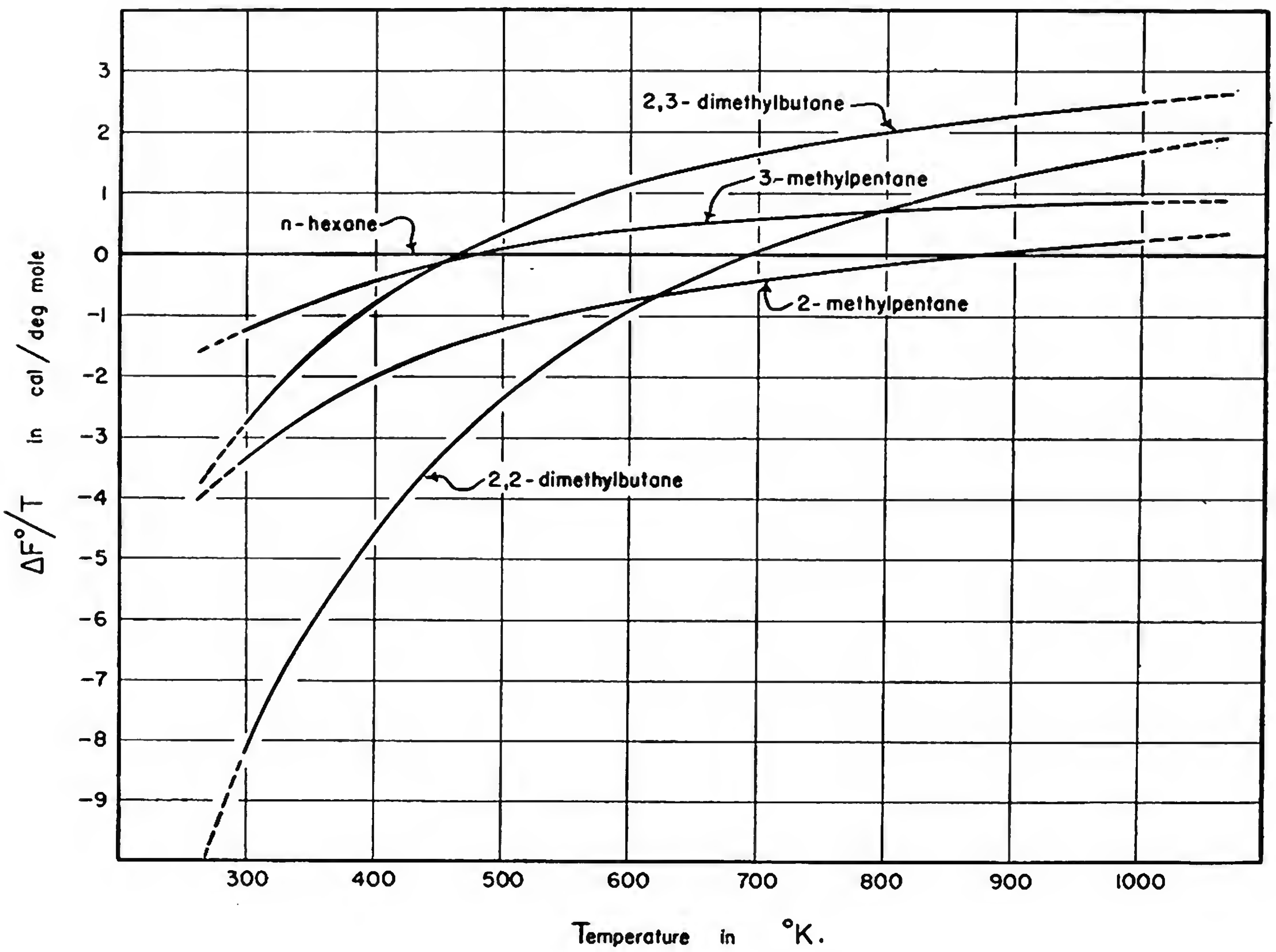

2,3- dimethylbutane
3-methylpentane
n-hexane
2-methylpentane
2,2-dimethylbutane
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
300
400
500
600
700
800
900
1000
ΔF°/T in cal / deg mole
Temperature in °K.

Fig. 3.

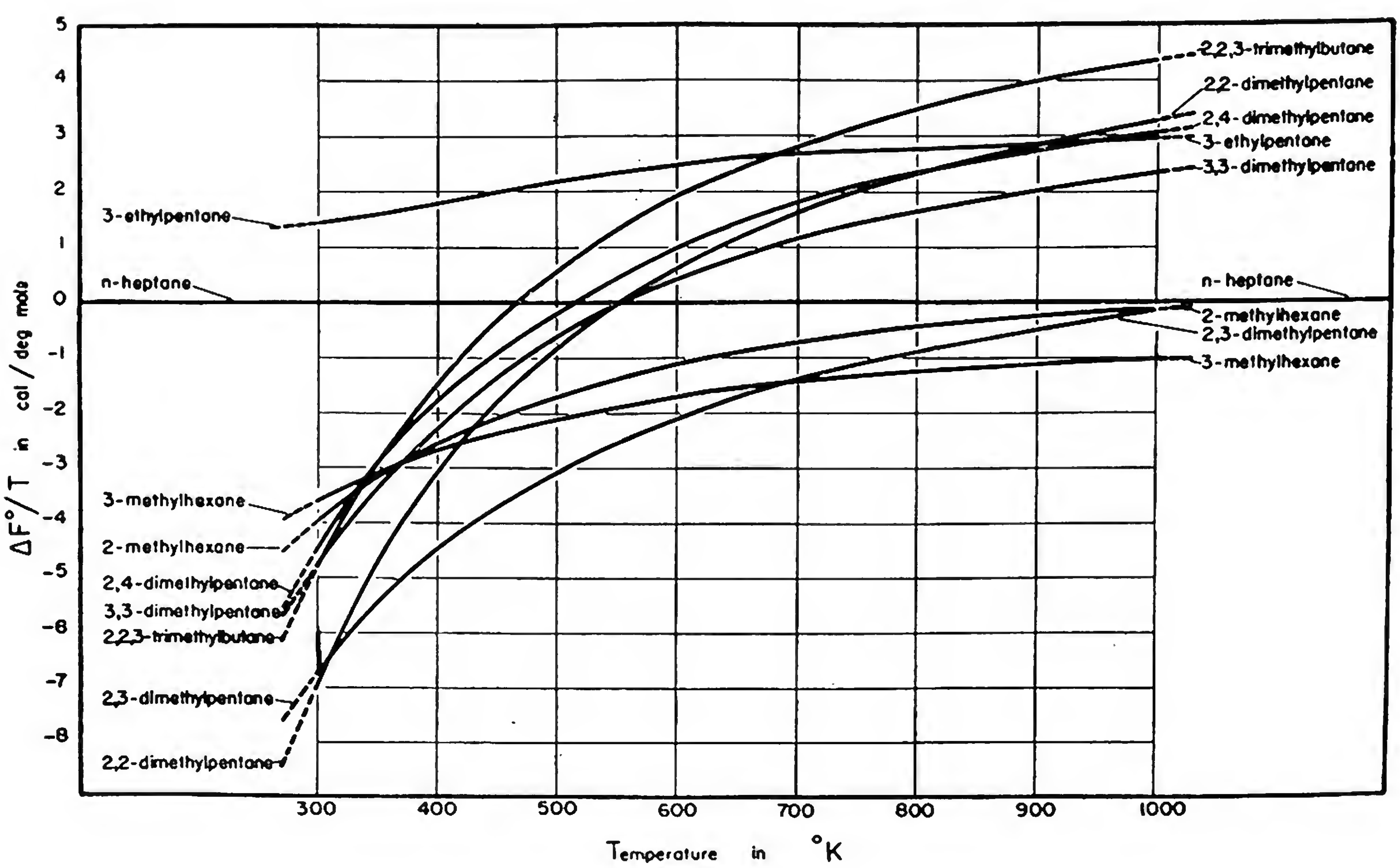

2,2,3-trimethylbutane
2,2-dimethylpentane
2,4-dimethylpentane
3-ethylpentane
3,3-dimethylpentane
3-ethylpentane
n-heptane
n-heptane
2-methylhexane
2,3-dimethylpentane
3-methylhexane
3-methylhexane
2-methylhexane
2,4-dimethylpentane
3,3-dimethylpentane
2,2,3-trimethylbutane
2,3-dimethylpentane
2,2-dimethylpentane
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
300
400
500
600
700
800
900
1000
ΔF°/T in cal / deg mole
Temperature in °K

Fig. 4.

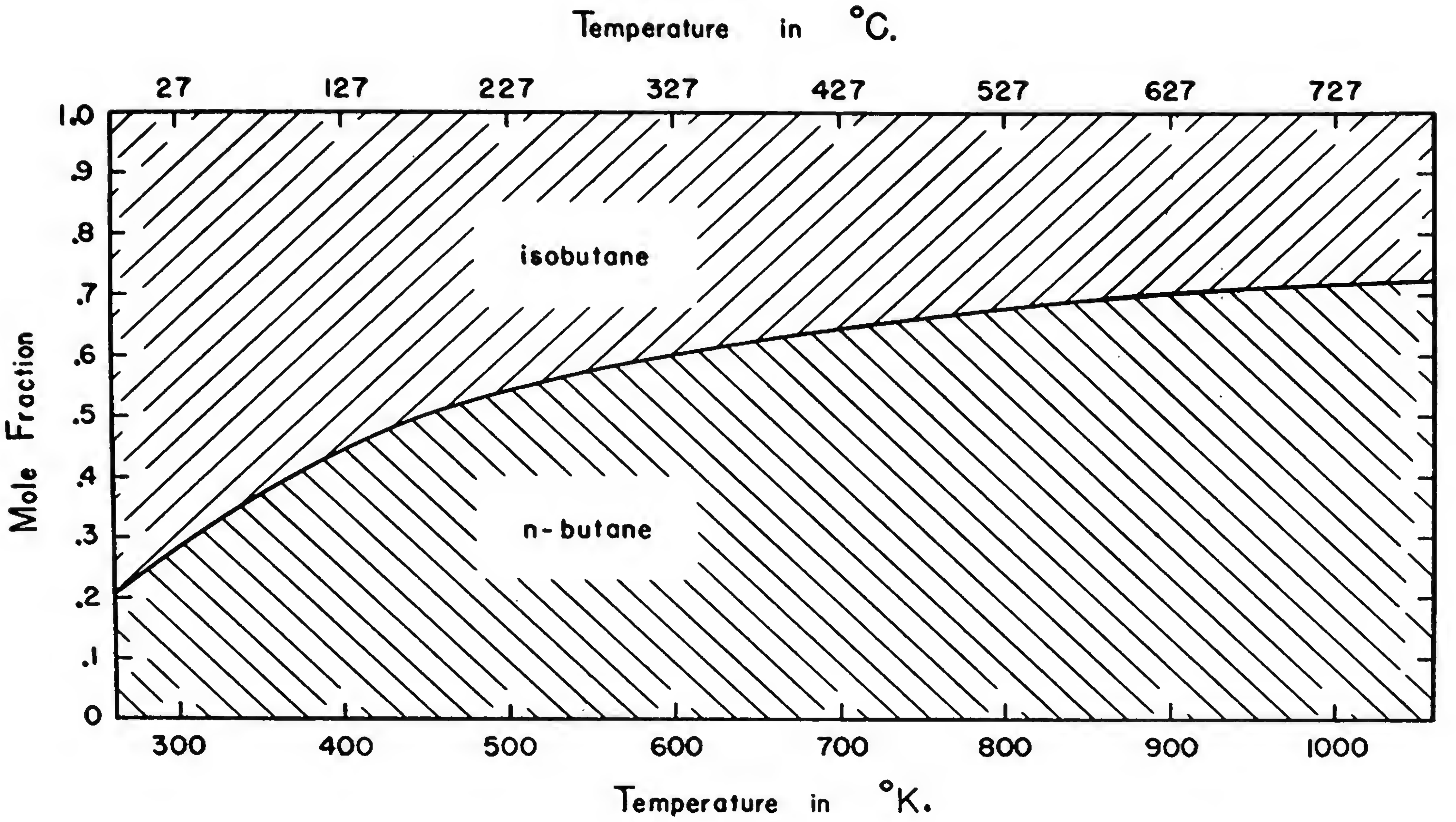

Temperature in °C.
27
127
227
327
427
527
627
727
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
Mole Fraction
isobutane
n-butane
300
400
500
600
700
800
900
1000
Temperature in °K.

FIG. 5.

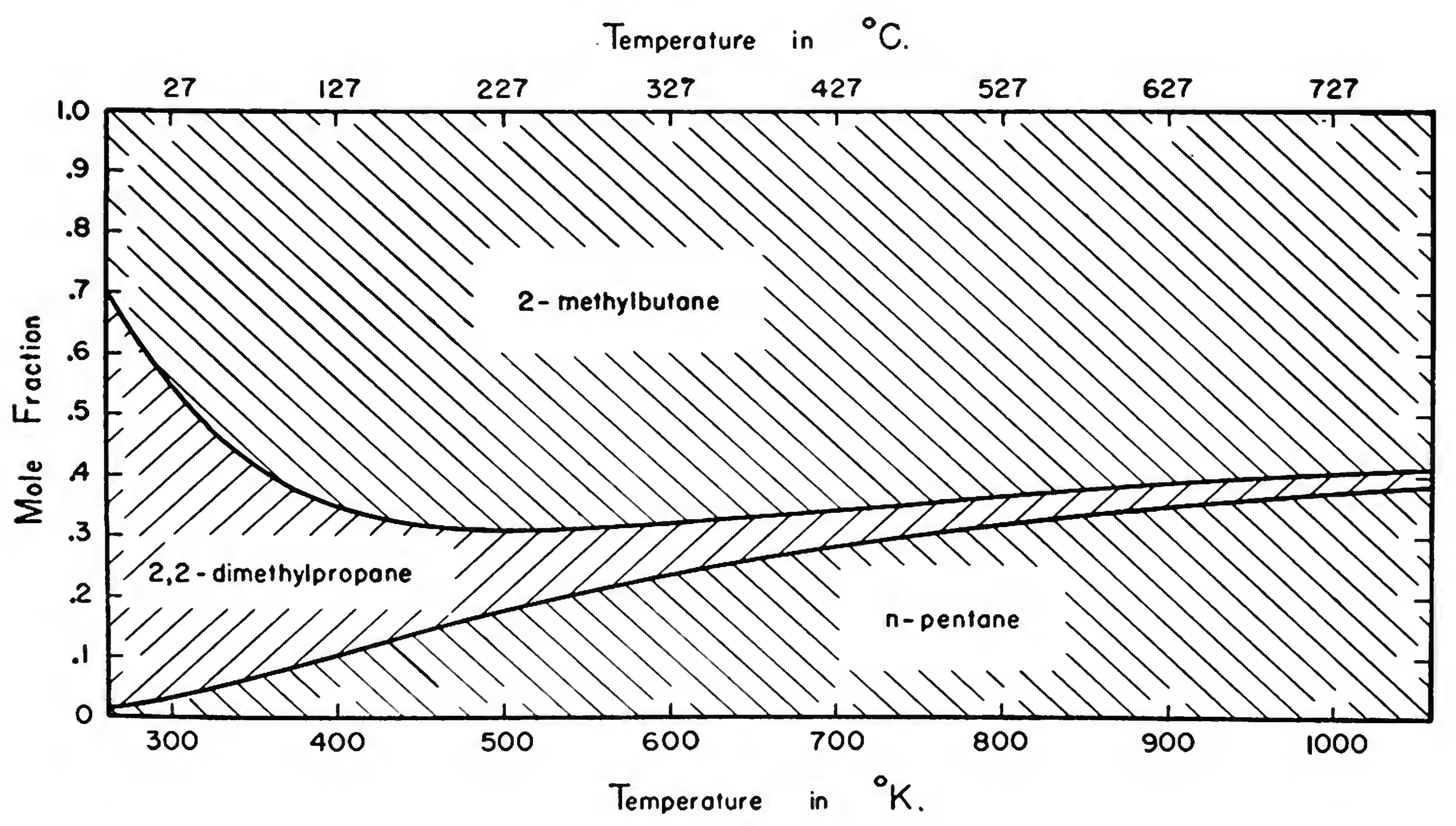
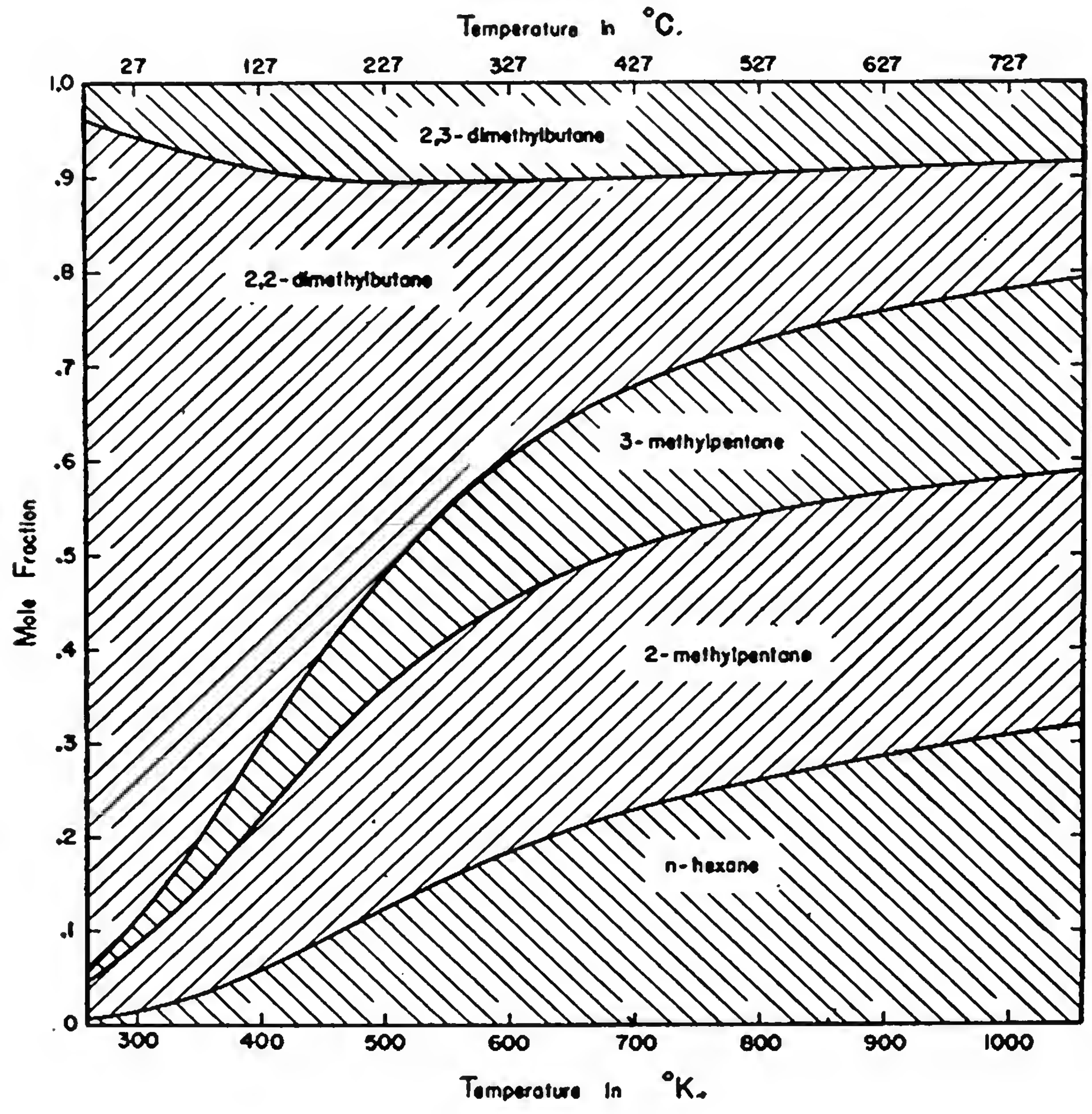
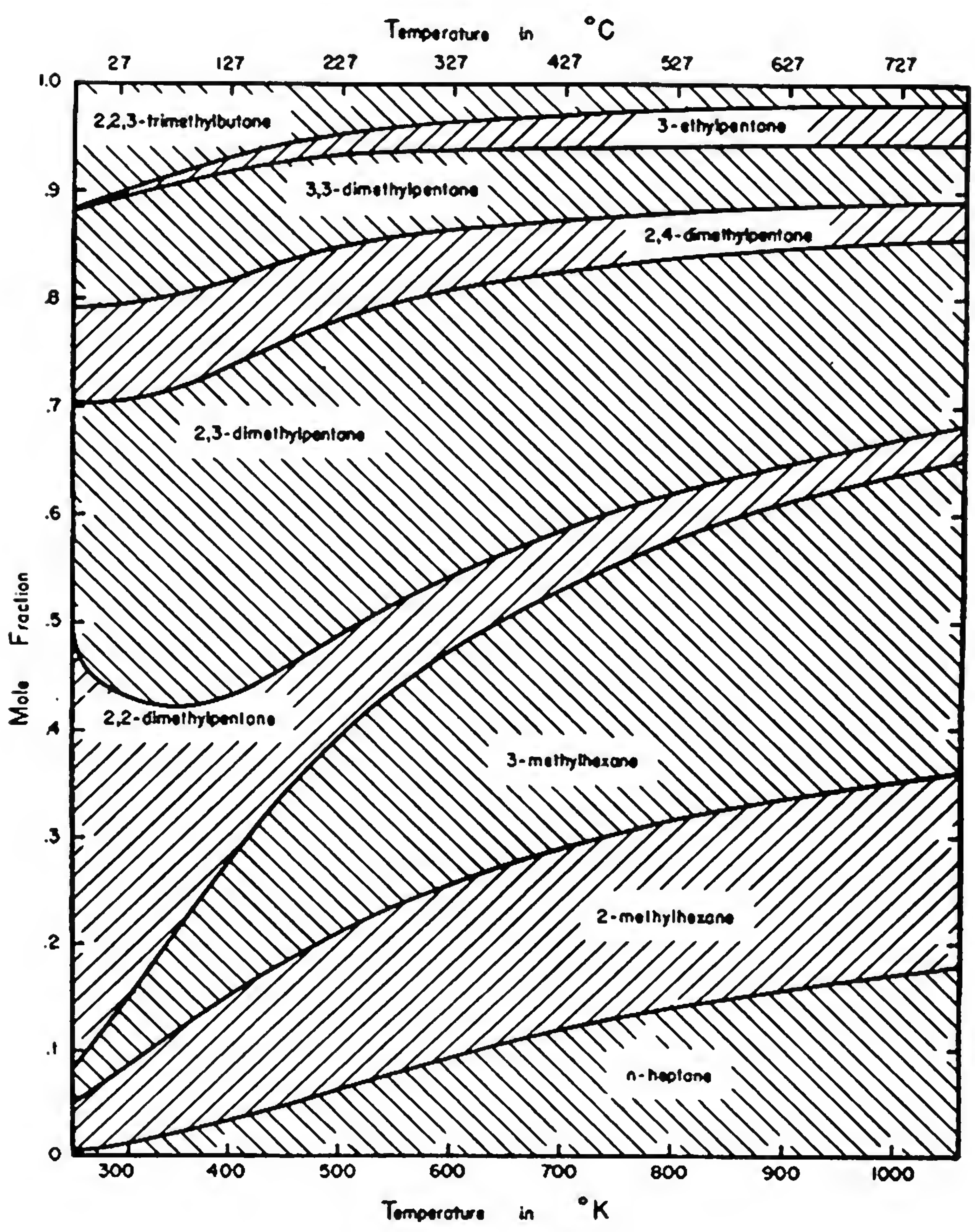

Temperature in °C.
27
127
227
327
427
527
627
727
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
Mole Fraction
2-methylbutane
2,2-dimethylpropane
n-pentane
300
400
500
600
700
800
900
1000
Temperature in °K.

FIG. 6.



Temperature in °C.
27
127
227
327
427
527
627
727
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
Mole Fraction
2,3-dimethylbutane
2,2-dimethylbutane
3-methylpentane
2-methylpentane
n-hexane
300
400
500
600
700
800
900
1000
Temperature in °K.

Fig. 7.



Temperature in °C
27
127
227
327
427
527
627
727
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
Mole Fraction
2,2,3-trimethylbutane
3-ethylpentane
3,3-dimethylpentane
2,4-dimethylpentane
2,3-dimethylpentane
2,2-dimethylpentane
3-methylhexane
2-methylhexane
n-heptane
300
400
500
600
700
800
900
1000
Temperature in °K

Fig. 8.

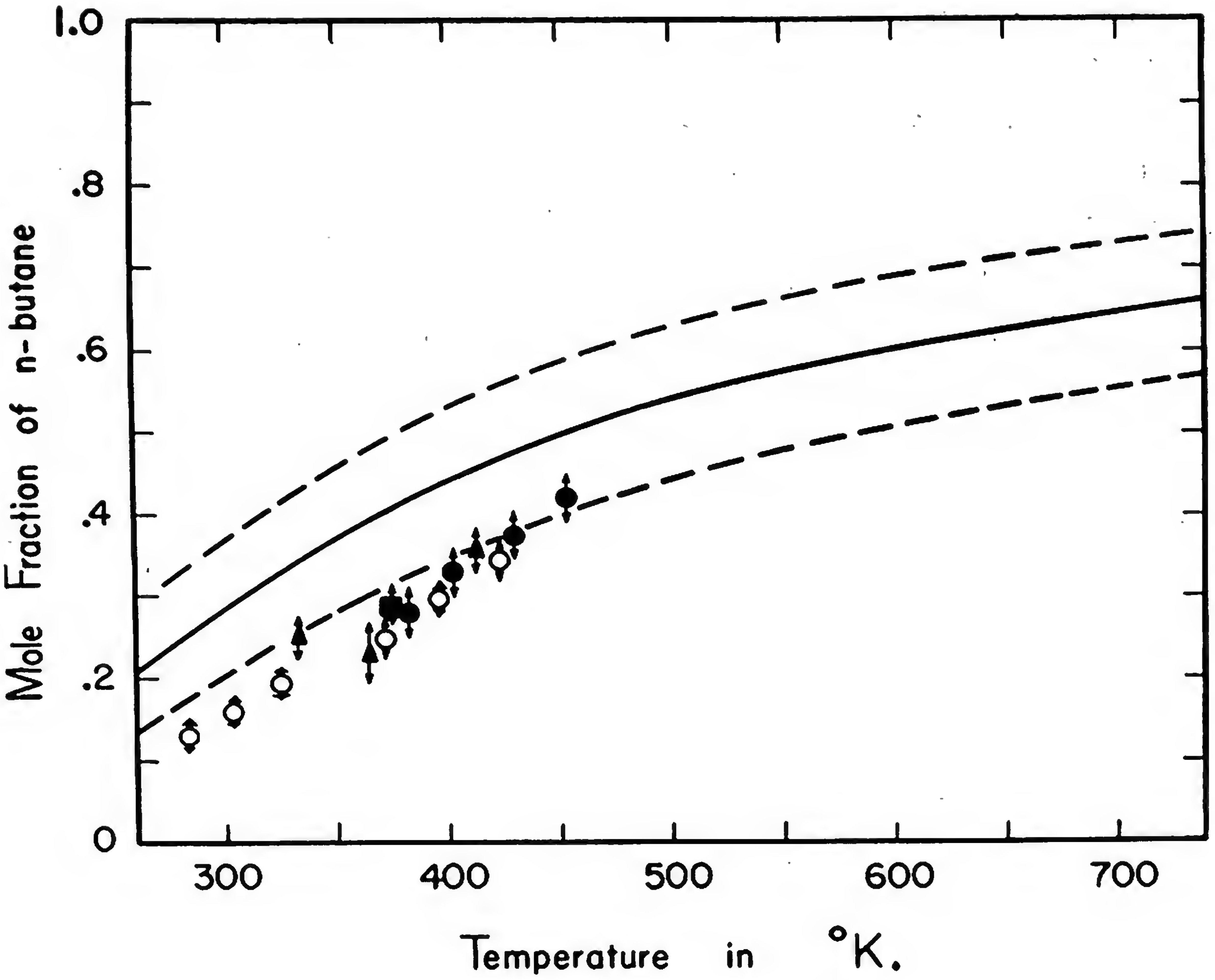


FIG. 9.

○ = Montgomery, McAteer, and Franke.[384, 385] Also Thorne.[477b]
● = Moldavsky and Nisovkina.[382]
▲ = Schuit, Hoog, and Verheus.[529a]
■ = De Simo, McMillan, and Cheney.[135a]

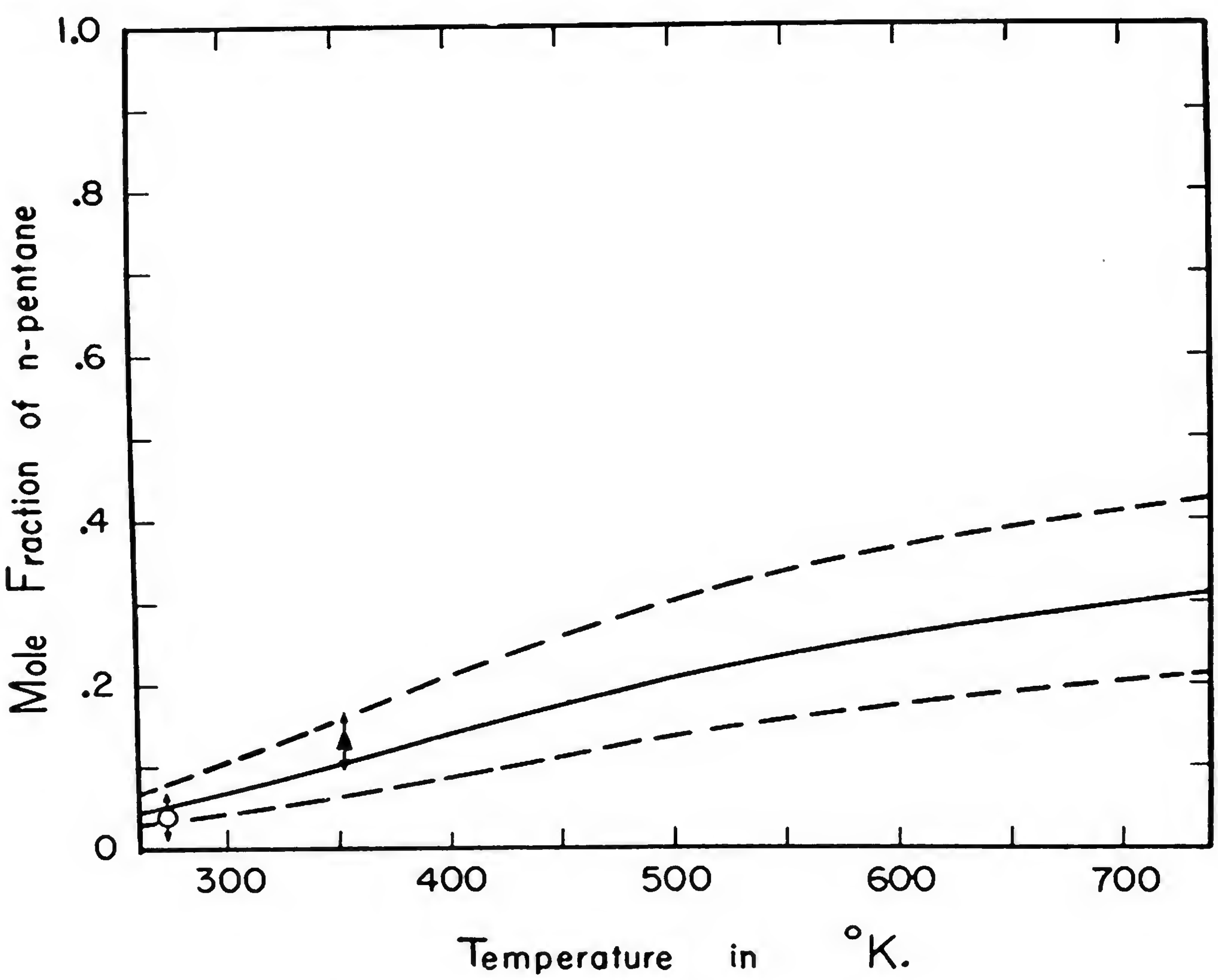


FIG. 10.

stability with increase in temperature, over the range 298 to 1000° K., and, at the latter temperature, is among the most stable of the isomers.

"(c) At 25° C., the 2,2-dimethyl isomer is in each case the most stable, but it rapidly becomes less stable with increasing temperature and at 1000° K. is among the least stable of the isomers."

The experimental data on all known isomerizations of alkanes, occurring in the presence of aluminum halides and other catalysts, are presented in Table 6, p. 218.

Conclusions

(1) Catalytic isomerization of alkanes proceeds by a change in the molecular configuration such that methyl groups are apparently transferred.

(2) Aluminum halides are, to date, the most effective catalysts for isomerization of alkanes.

(3) Isomerization of alkanes is generally accompanied by the formation of hydrocarbons with lower and higher carbon contents.

Chapter II

Alkenes, Alkadienes, and Alkapolyenes

The aliphatic hydrocarbons with double bonds to be discussed in this chapter are: alkenes, allenic alkadienes, non-allenic alkadienes, and alkapolyenes (cyclenes will be considered in Chapter V).

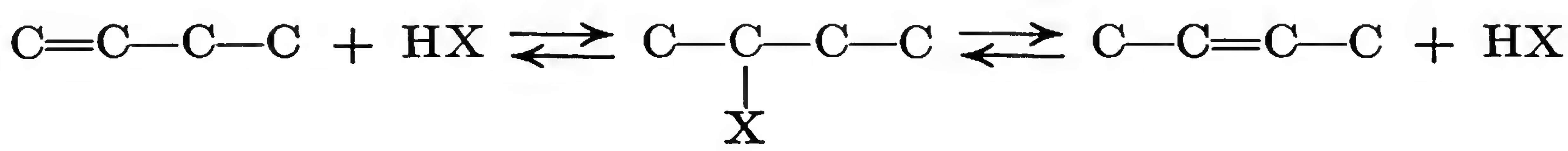
Isomerization of Alkenes

Mechanism

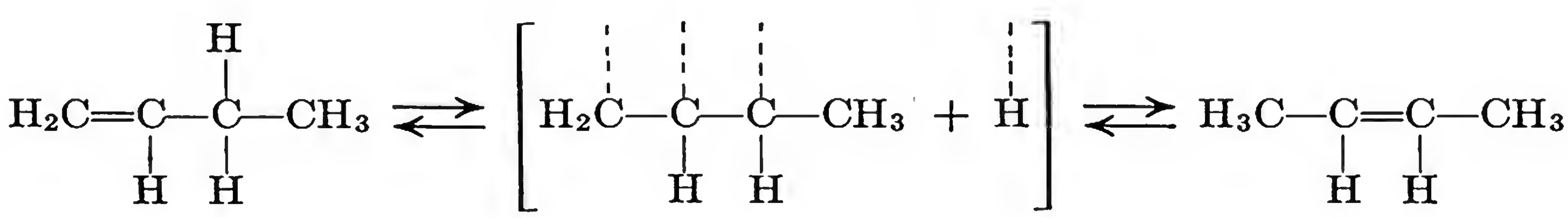
Isomerization of alkenes may proceed in several directions:

1. **Isomerization by shift of a double bond.** This change occurs theoretically in one or more ways, *e.g.*,

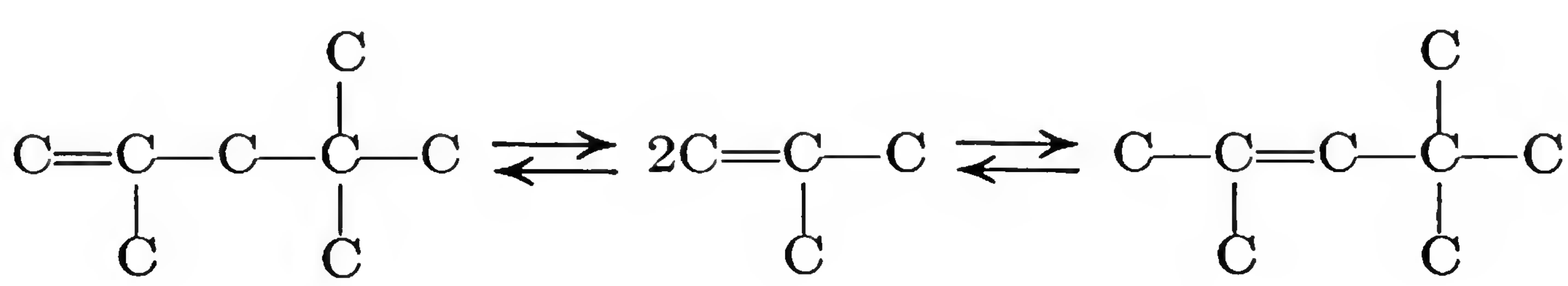
(a) by the formation of an unstable intermediate product:



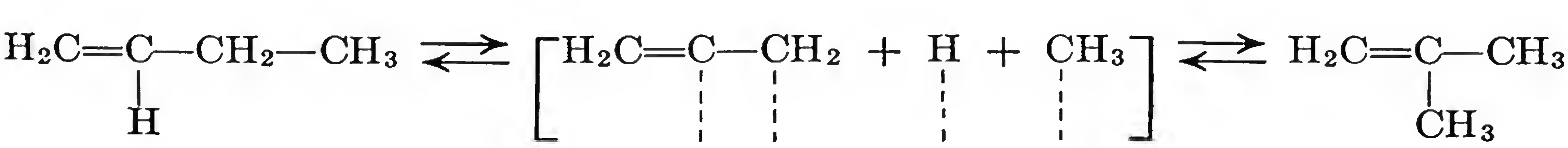
(b) by the occurrence of free radical processes (the broken lines represent residual valences assignable to the radicals):



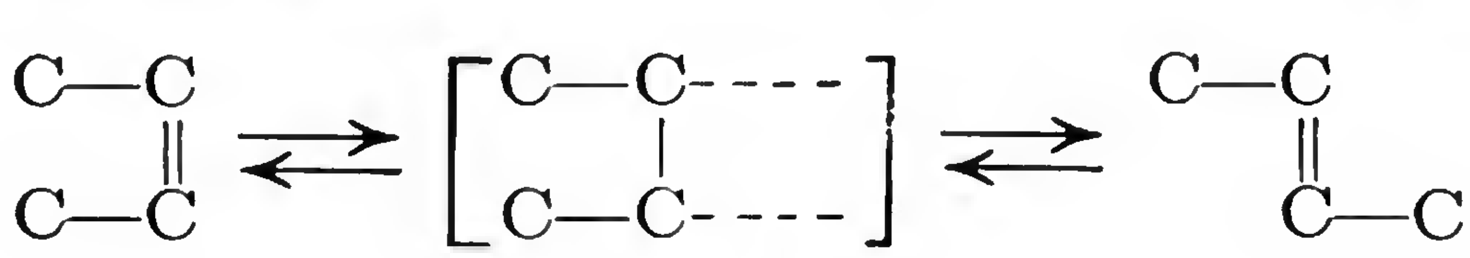
(c) by depolymerization plus polymerization (both hypothetical reactions):



2. **Isomerization by change in chain branching alone.** This occurs theoretically through a free radical exchange, *e.g.*,

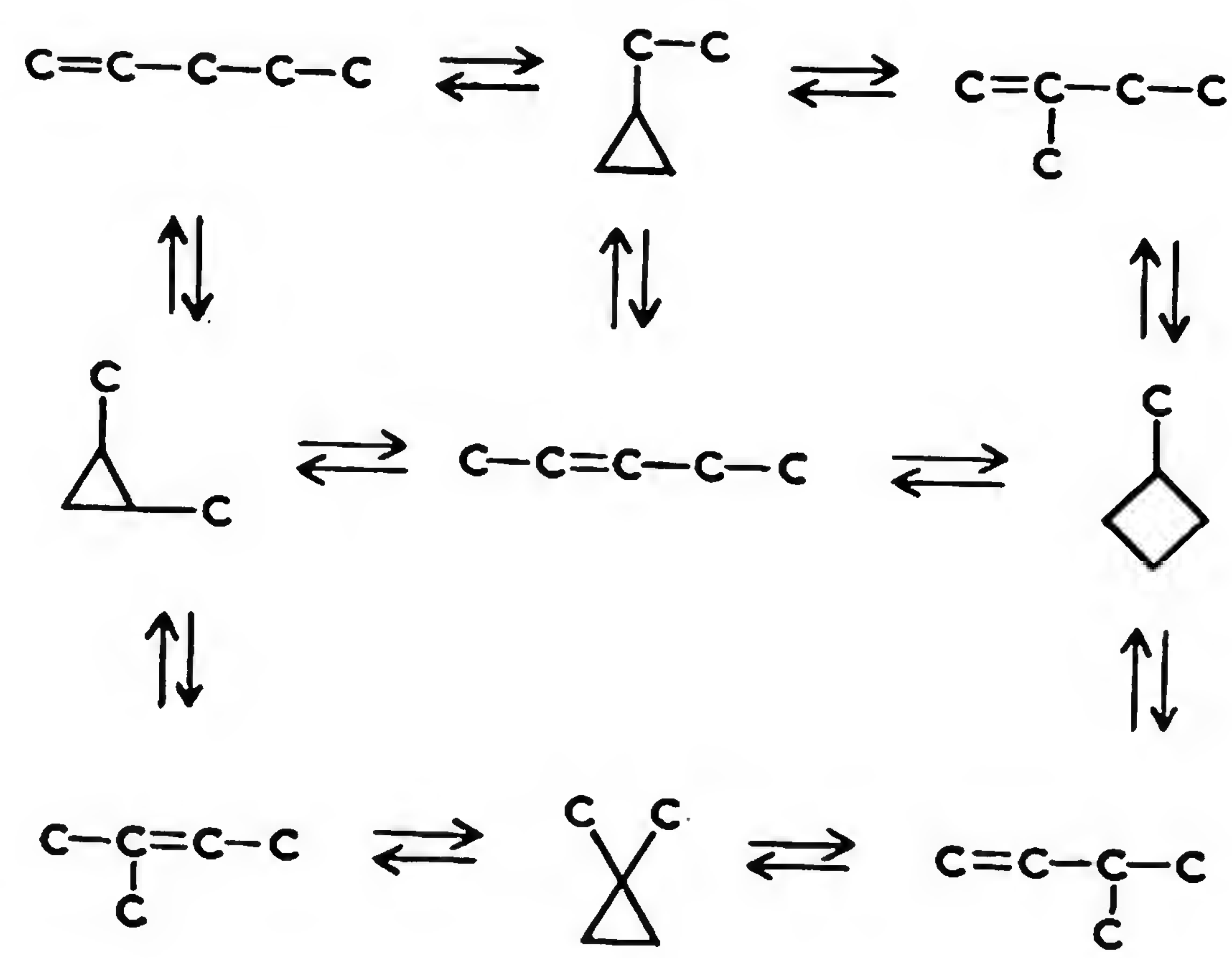


3. **Isomerization by interconversion of cis and trans isomers,** *e.g.*,



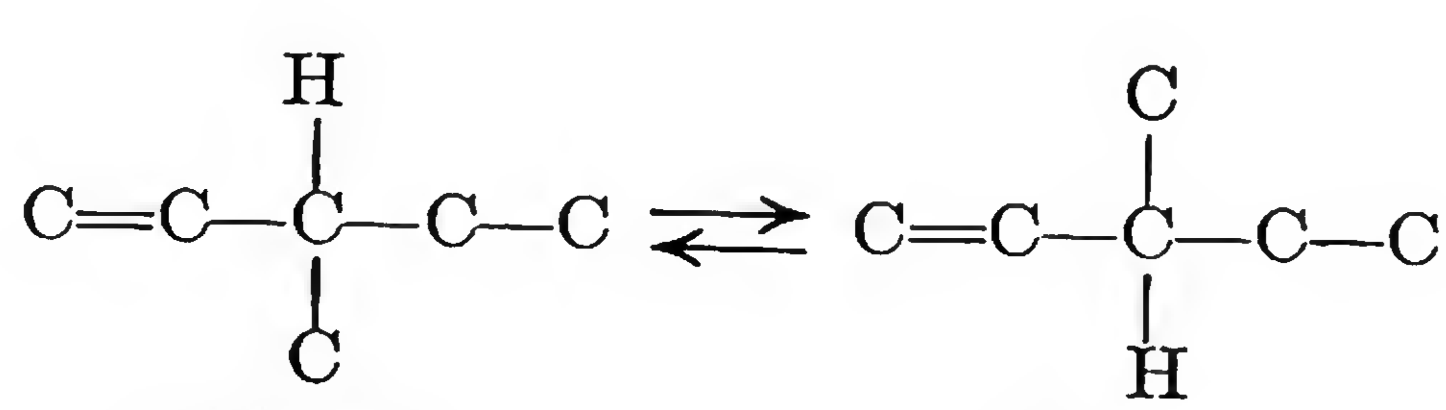
4. **Isomerization by cyclization, or "internal" alkylation.** This results in the formation of a cyclane, *e.g.*,

5. **Isomerization by hydrogen transfer plus cyclization, followed by decyclization plus hydrogen transfer.** The isomers are formed by variable branching and cyclization, *e.g.*,



6. **Isomerization by polymerization plus intermediary isomerization of the polymer plus depolymerization.** This sequence of reactions seems quite probable, but has not been studied to date.

7. **Isomerization by change in arrangement of the 4 different groups about an asymmetrical carbon atom.** The following case would be the simplest.



[*d*-form] [*l*-form]

Isomerization of the alkenes, proceeding in any of the first 6 preceding directions, requires a shift of the hydrogen atom (except in those rare and as yet unstudied cases where such hydrogen is replaced by an alkyl). Formation of isomers according to directions 2, 5, and 6 requires the "rupture" of a C—C bond as well. This occurs either in the manner of isomerization of alkanes or by the formation of a short-lived cyclane.

It may be pointed out that whenever a transfer of a hydrogen atom takes place, resulting in the shift of a double bond, a three-carbon or allylic-type isomerization is apparently involved. This process may be

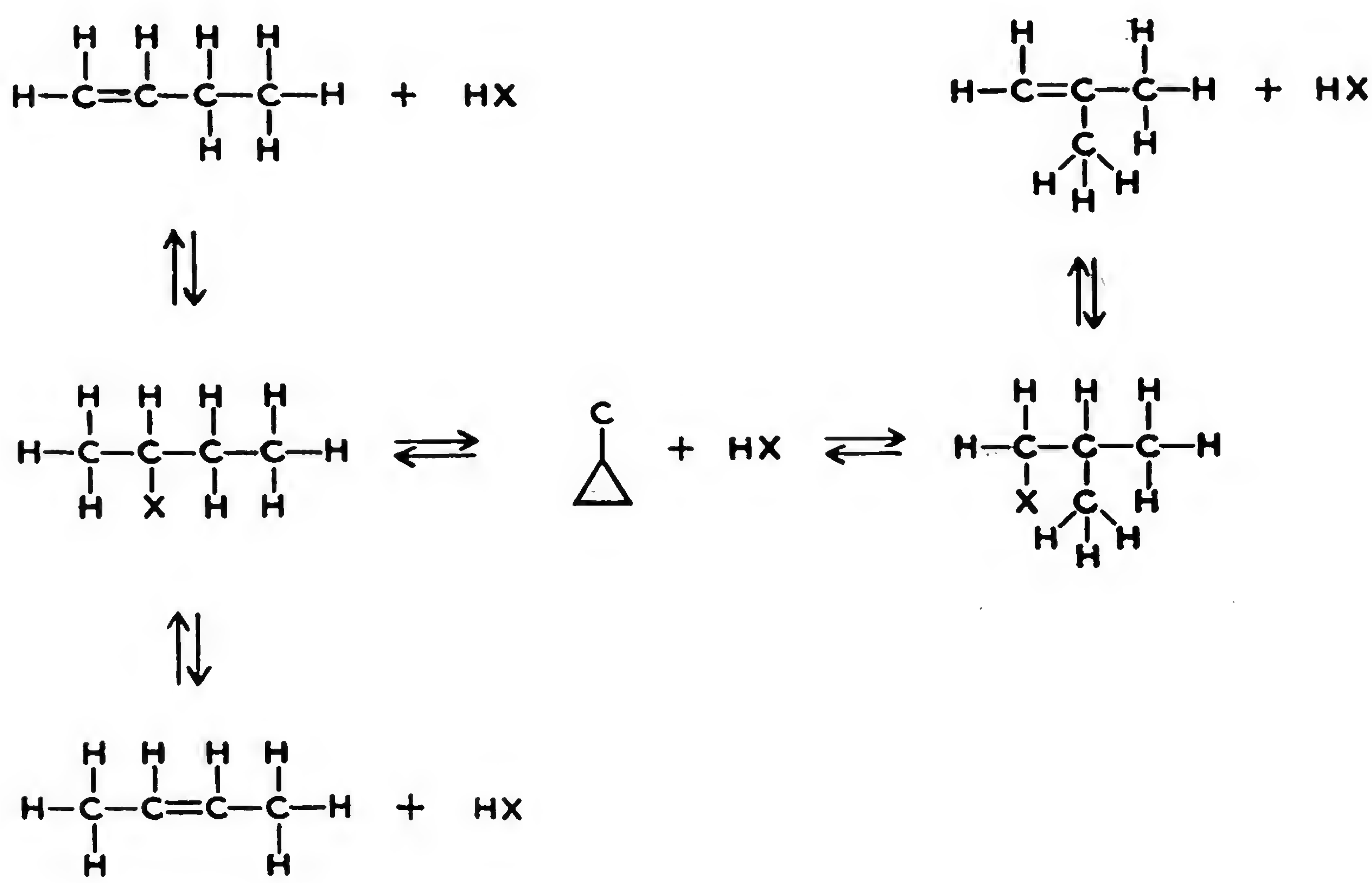
repeated if the molecule is a long one. The mechanism of an acid-catalyzed double-bond shift consists of 2 steps:[285]

(1) Formation of an addition product from the alkene and the catalyst, and

(2) Decomposition of the addition product, whereby the same alkene or one with a different structure is split off, and the catalyst regenerated. The reaction can be formulated as follows:[285]

$$H_2C{=}CHCH_2CH_3 + HX \rightleftarrows \underset{\displaystyle X}{CH_3\overset{}{C}HCH_2CH_3} \rightleftarrows CH_3CH{=}CHCH_3 + HX,$$

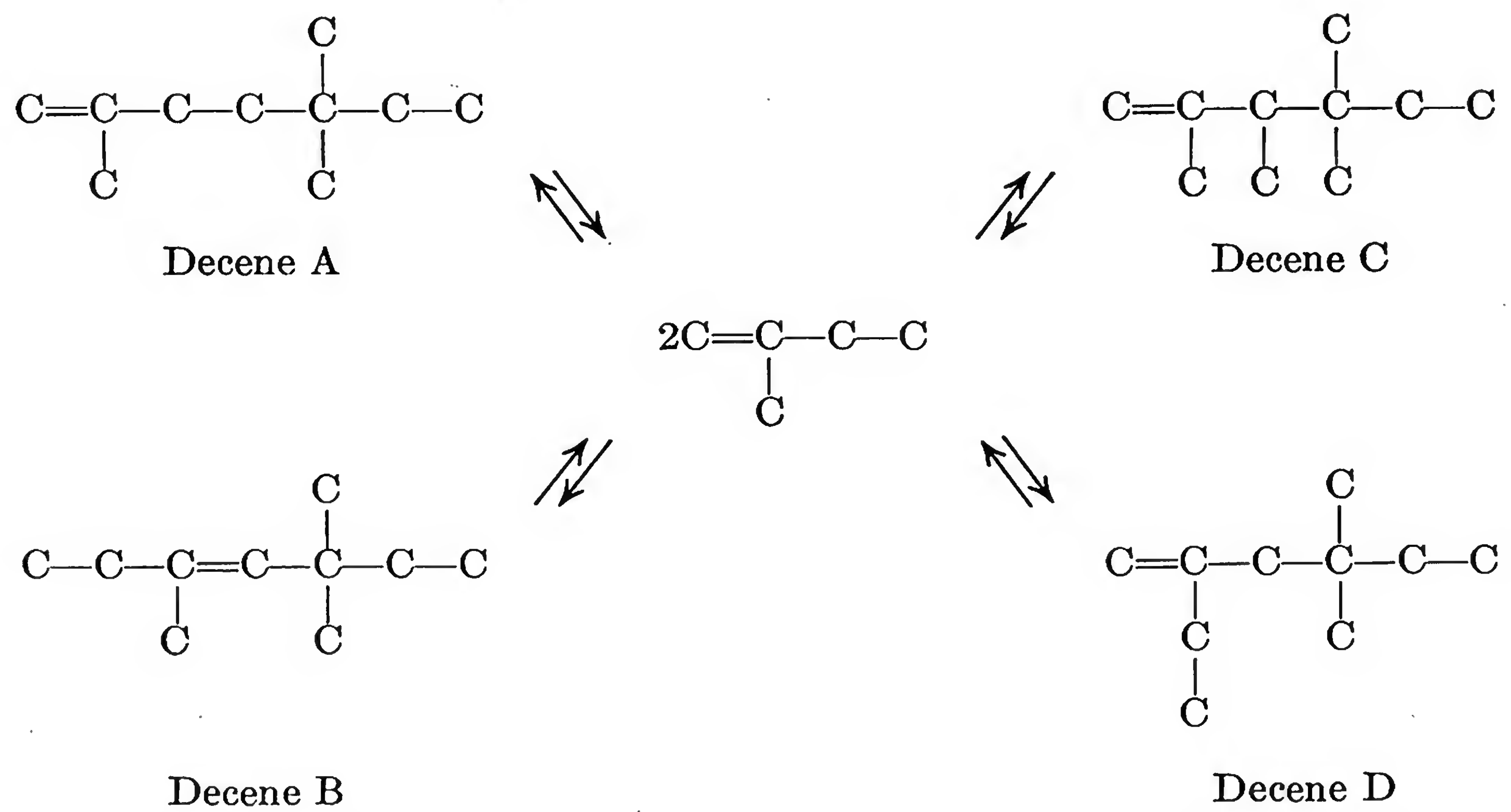
where "X" represents a negative group. This mechanism can be used for the interpretation of the isomerizations involving a short-lived cyclane or yielding a stable one. This requires the preliminary removal of hydrogen from a carbon atom which is more remote to the "X" group, *e.g.*:



The postulated cyclizations are actually intramolecular alkylations in which part of the molecule is alkylated either by a condensation within an ester or through the addition upon the double bond (direction 5). The conversion of a short-lived cyclane into its isomers may proceed without the catalyst, HX, by an alternative thermal isomerization. In all these cases the decyclization of a short-lived cyclane is the reverse process of "dealkylation" into an alkene.

Isomerization of alkenes by change of carbon-chain configuration (direction 2) may be at times the result of a destructive alkylation, or depolymerization plus polymerization (direction 1c). Thus, depolymerization of any of the following decenes A, B, C, or D into 2-methyl-

butene-1, followed by polymerization, should lead largely to isomer formation with a change in branching:



The mechanism of alkene isomerization in still other cases may approach that of the alkanes, especially when changes occur in those parts of the alkene molecule remote from the double bond.

The alkenes are characterized by a tendency to polymerize, which must be taken into account in isomerization processes. The conditions of isomerization and the catalysts applied are preferably mild, in order to avoid formation of polymers. Furthermore, the temperatures used in

Table 7. Number of Structurally Isomeric Hydrocarbons of the Alkene Series. (Excluding the additional isomers due to stereoisomerism)

From Henze and Blair[248]

Carbon content	Number of isomers
2	1
3	1
4	3
5	5
6	13
7	27
8	66
9	153
10	377
11	914
12	2,281
13	5,690
14	14,497
15	36,564
16	93,650
17	240,916
18	623,338
19	1,619,346
20	4,224,993

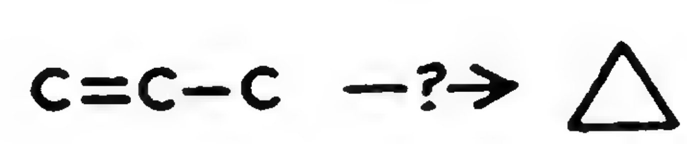
Note: The correct number of $C_{14}H_{28}$ isomers is 14,397, according to Henze and Blair.[249]

catalytic isomerization are close to those in cracking and polymerization.[437] In reactions carried out with strong catalysts (*e.g.*, aluminum halides), as well as at high temperature, very little isomerization takes place. It is then accompanied or succeeded by other reactions (*e.g.*, polymerization, hydrogen disproportionation, and alkylation).

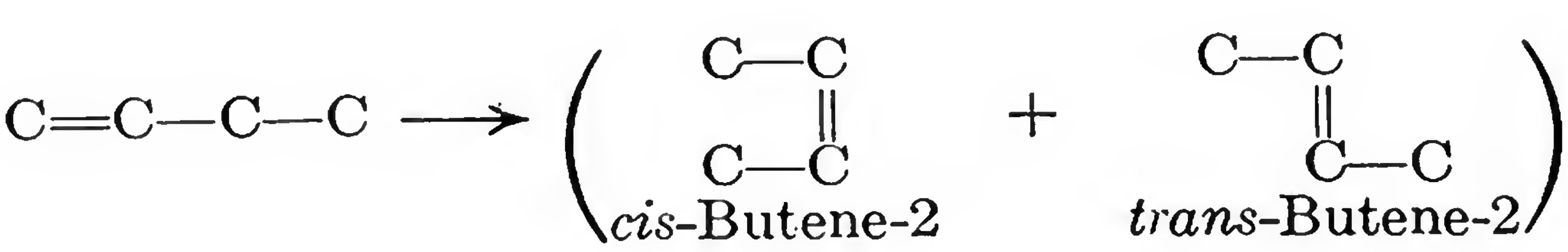
Identification of the alkene isomers is facilitated by their chemical activity, as contracted to the alkanes. A suitable method of identification of *cis-trans* alkene isomers is a simple reaction-rate measurement using alkene dibromides and potassium iodide.[658] The *cis* and *trans* forms of butene-2 have widely different coefficients of thermal conductivity; these isomers, therefore, may be analyzed by means of the Pirani gauge.[600a] The number of structurally isomeric alkenes (Table 7) greatly exceeds that of the alkanes with the same content of carbon atoms per molecule.

Isomerizations

Propene. The conversion of cyclopropane into propene is a well-established fact. However, the isomerization of propene by cyclization to cyclopropane has been reported only twice: (1) the heating of propene at 400-405°, whereby more than 50 per cent of a product containing cyclopropane was obtained,[166] and (2) the formation of about 60 per cent of cyclopropane from propene at 410°.[203] Some workers cast grave suspicions on this observation by pointing out the highly-strained condition of cyclopropane and the consequent unfavorable equilibrium states.[590]



Butenes. Butene-1, passed through a quartz tube at 550°, gave butene-2 (87 per cent) without formation of isobutene.[266,267] In another case, butene-1 at 650° gave a butene *fraction* containing high-boiling butene-2 (8 per cent), low-boiling butene-2 (13 per cent), and butene-1 (79 per cent).[264] Hence, butene-2 is formed in the proportion of 38 per cent of the *cis* form (high-boiling, reported incorrectly as *trans*) to 62 per cent of the *trans* form . At 700° the butene fraction has 16 per cent of butene-2 and 84 per cent of butene-1. Isobutene was absent in all cases.[264]



Various catalysts [285] permit the conversion of butene-1 into butene-2 at much lower temperatures. Solutions of zinc chloride (75 per cent at 100°), benzenesulfonic acid (75 per cent at 76°), and perchloric acid (71 per cent at 21°) gave 5, 13, and 21 per cent of butene-2 at atmospheric pressure, respectively. Pure phosphoric acid at atmospheric pressure con-

verted butene-1 into butene-2 to the extent of 12 per cent at 78° and 60 per cent at 135°. Phosphoric acid, on diatomaceous earth, catalyzed a complete conversion of butene-1 to butene-2 at 249° and 7.8 atmospheres' pressure. The reaction efficiency decreases upon lowering the temperature.

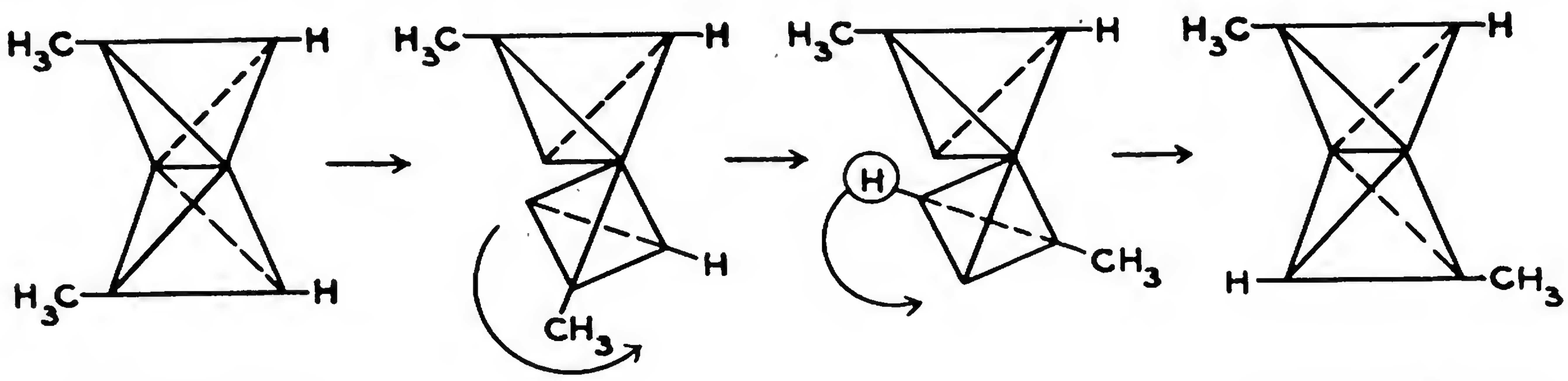
Isomerization of butene-1, within lime-filled porcelain tubes, at 420° yields 92 per cent of butene-2.[266, 267] Catalysts, such as bauxite, silica, titania, difficultly-reducible metal oxides, neutral borates, neutral phosphates, neutral silicates, and aluminum phosphate on pumice acted similarly at 400°.[266, 267] Aluminum sulfate was found to be effective also.[212] An isomerization of butene-1 into butene-2 occurs in the dehydration of butanol-1 over alumina and is probably due either to the catalytic action of traces of sulfuric acid[362] or to an accumulation on the catalyst of acidic materials resulting from oxidation (by traces of air introduced into the catalyst chamber during shut-down periods).[285] Butene-1 probably isomerizes to butene-2 upon interaction with an equal amount of hydrogen at 133° in the presence of nickel.[600] The formation of butene-2 was indicated only by a decrease in the vapor pressure of the product. The reaction does not occur in the absence of hydrogen and gives simultaneously 10 per cent of *n*-butane. Subsequent work indicates that the isomerization of butene-1 into butene-2 in the presence of hydrogen and fine nickel wire at 65° is reversible and proportional both to the square root of the total pressure of the butenes and to the square root of the hydrogen pressure.[600a] The equilibrium concentration of butene-2, approached from both sides at 65°, was found to be about 93 per cent of the total concentration of butenes. No isomerization occurred at 65° when hydrogen was absent in the initial butene-1, even though nickel was present. The following "associative mechanism" was proposed for the isomerization of butene-1:

$$\underset{\substack{|\\ Ni}}{CH_2}\text{–}\underset{\substack{|\\ Ni}}{CH}\text{–}CH_2\text{–}CH_3 + H \longrightarrow CH_3\text{–}\underset{\substack{|\\ Ni}}{CH}\text{–}CH_2\text{–}CH_3 + Ni \longrightarrow CH_3\text{–}\underset{\substack{|\\ Ni}}{CH}\text{–}\underset{\substack{|\\ Ni}}{CH}\text{–}CH_3 + H$$

The activation energy for the double-bond migration was given as 5.9 kilocalories per gram-mole of butene-2 formed at 76-126°.[600a]

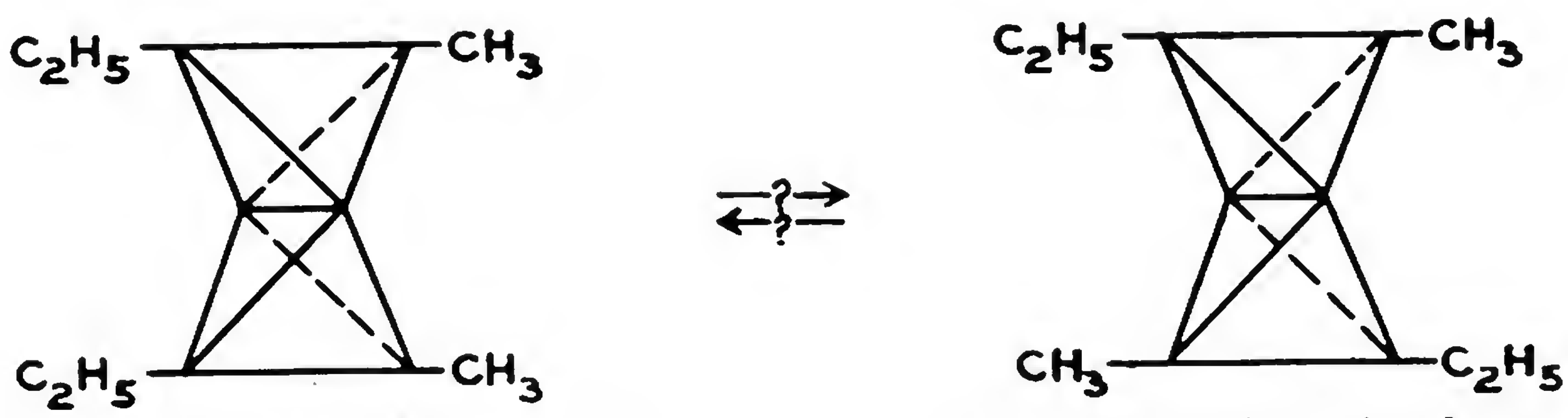
The isomerization of butene-2 is of special interest because of the existence of 2 forms, *cis* and *trans,* in this hydrocarbon. These forms occur because of two possible stereochemical arrangements of the terminal methyl radicals about an ethylene group. The methods of preparation, physical constants,[153] properties, electron diffraction measurements,[92] ultraviolet absorption spectra,[99] heat of hydrogenation,[305] and isomerization and addition reactions[581c] of butene-2, have jointly established the facts that the low-boiling butene-2 is the *trans* form and that the *cis-trans* isomerization is characteristic of certain alkenes.

The isomerization of *cis*- into *trans*-butene-2 and of *cis*- into *trans*-pentene-2 probably involves a transfer of hydrogen with the "opening and closing" of the double bond. Such a mechanism seems to be more plausible than the exchange of a hydrogen atom and an alkyl group. From this point of view, there cannot be a complete C—C break and a reunion in the isomerization of butene-2 and of pentene-2, but there is rather a *partial break* followed by a *rotation*:



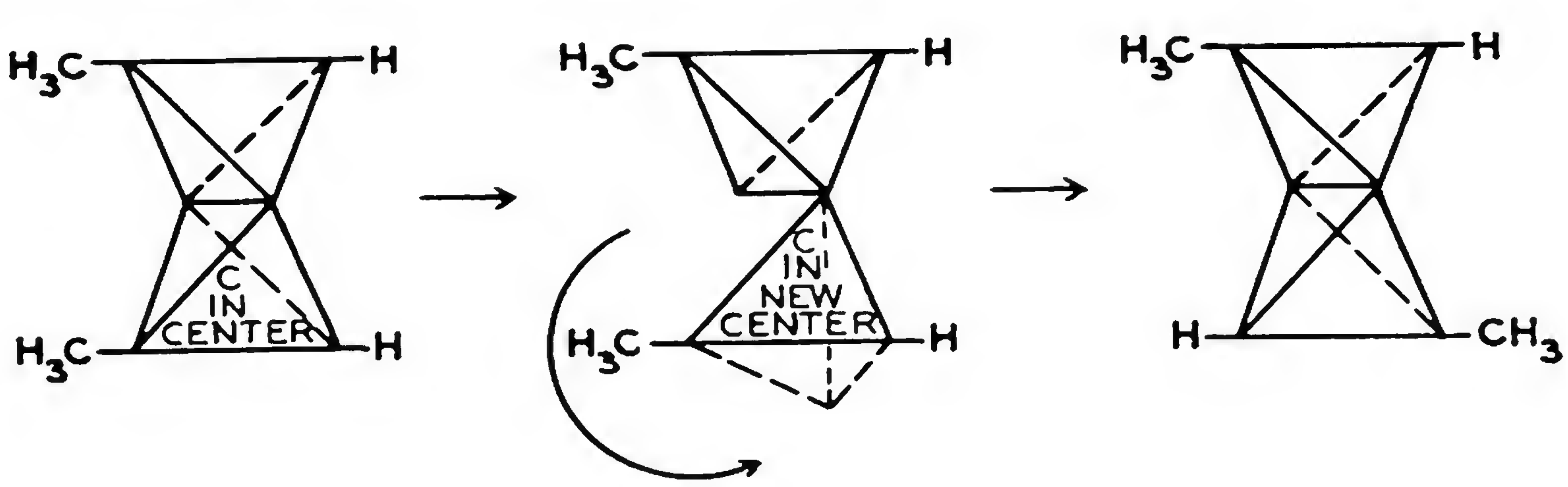
cis-Butene-2 *trans*-Butene-2

On account of this mechanism, the question arises whether it is possible to have a *cis-trans* isomerization of tetra-alkyl ethylenes, wherein no labile hydrogen occurs about the double bond, as in the case of *cis*-3,4-dimethylhexene-3:



cis-3,4-Dimethylhexene-3 *trans*-3,4-Dimethylhexene-3

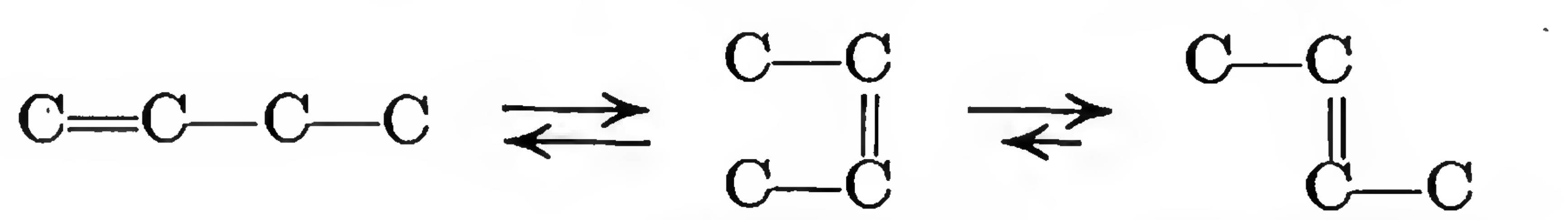
An alternative explanation of the isomerization of *cis*- into *trans*-butene-2 involves a 180° redistribution of the electronic charge about one particular carbon atom (actively involved in the "opening" of the double bond). This carbon atom forms the basis of a "new tetrahedron," and is followed by a 180° rotation. In this case, a labile hydrogen atom or labile alkyl group would be unnecessary.



The idea of a "new tetrahedron" is used in organic chemistry to explain such reactions as the Walden inversion [350] and the photochemical isomerization of *cis*-cinnamic acids.[64]

The *cis-trans* isomerization of butene-2 has an equilibrium constant near 1.12 at 390°, corresponding to 52.8 per cent of the *trans* isomer.[307] A study of kinetics in the conversion of *cis-* into *trans*-butene-2 at 390-420° has indicated a homogeneous reaction of approximately first order.[307] However, it has been pointed out that a bimolecular mechanism is equally justifiable as an interpretation of the data.[241]

A mixture of 38 per cent high-boiling (*cis*) and 62 per cent low-boiling (*trans*) butene-2, heated at 650° and 700°, gave butene fractions containing isomers.[264] These fractions contained 16 and 30 per cent of butene-1, respectively; butene-2 was present but isobutene was absent. The recovered butene-2 contained 39 per cent of the *cis* and 61 per cent of the *trans* form. This isomerization of butene-2 at elevated temperatures is the reverse reaction of that observed in the case of butene-1. Hence, an equilibrium relationship exists between butene-1 and the *cis-trans* forms of butene-2. The mechanism of the formation of butene-1 probably involves dislocation of the double bond in *cis*-butene-2 (rather than the *trans* form). This statement is contingent upon there being a higher energy content in *cis* forms (over *trans*) at elevated temperatures. The equilibrium relationships would then assume the following order:



cis-Butene-2 *trans*-Butene-2

cis-Butene-2 (erroneously reported as *trans*) was partially isomerized into the *trans* form (6 per cent) and into butene-1 (6.6 per cent) in the presence of pure phosphoric acid at 100° and atmospheric pressure.[285] Subsequently, the exothermic heats of hydrogenation of butene-1, *cis*-butene-2, and *trans*-butene-2 at 82° were found to be 30.341 ± 0.025, 28.570 ± 0.019, and 27.621 ± 0.021 kilocalories per gram-mole, respectively.[304a] Subtraction of these heat quantities, that of *cis*-butene-2 being the minuend, gives -1.771 ± 0.031 and $+0.949 \pm 0.028$ kilocalories per gram-mole as the "heat of isomerization" of *cis*-butene-2 at 82° into butene-1 and into *trans*-butene-2, respectively. These values indicate the occurrence of (1) an endothermic or unfavorable isomerization of *cis*-butene-2 into butene-1, and (2) an exothermic, or much more probable, conversion of *cis*-butene-2 into the *trans* form.

n-Butenes are isomerized to isobutene at 294° in the presence of steam and a catalyst such as alumina, aluminum sulfate, Glukhov clay, "floridin," or phosphoric acid dried either on charcoal or "silicate" related to chamotte.[199, 200] In this isomerization, polymers and gaseous alkanes were formed also. Likewise, a catalyst prepared by heating phosphoric acid with kieselguhr to 300° catalyzes the conversion of butene-1 and butene-2 into isobutene at about 325°.[420, 421] A related patent reports

a 33 per cent yield of isobutene.[417] Phosphoric acid on kieselguhr catalyzes the conversion of n-butenes into isobutene at temperatures from 325° down to 250°, but butene-1 at temperatures below 250° yields butene-2 instead of isobutene.[609a]

$$\mathrm{C{=}C{-}C{-}C} \longrightarrow \mathrm{C{=}\underset{\displaystyle |\atop \displaystyle C}{C}{-}C} \longleftarrow \mathrm{C{-}C{=}C{-}C}$$

A series of experiments [540] is concerned with the equilibrium relationship between isobutene and a feed mixture of butene-1 (27 per cent), *cis*-butene-2 (29 per cent), and *trans*-butene-2 (44 per cent) at 265-426° in the presence of phosphoric acid dried on chamotte. It was found that the equilibrium concentration of isobutene at 300° is about equal to that of butene-1 plus butene-2, and that it decreases with rise in temperature in accordance with the following equation:[199, 540]

$$\log_{10} K_p = \log_{10} \frac{\text{Isobutene}}{\text{Butene-1} + \text{Butene-2}} = \frac{304}{T} - 0.528$$

A comparison between the observed (304 multiplied by $R \log_e 10$) and calculated values of the heat of isomerization, Q, of n-butenes into isobutene is instructive:

Butene-1	$Q = 3.582$ kilocal./gram-mole	(calc. for 25-82°)
cis-Butene-2	$Q = 1.811$ kilocal./gram-mole	(calc. for 25-82°)
trans-Butene-2	$Q = 0.862$ kilocal./gram-mole	(calc. for 25-82°)
n-Butenes (stated mixture)	$Q = 1.87$ kilocal./gram-mole	(calc. for 25-82°)
n-Butenes (stated mixture)	$Q = 1.39$ kilocal./gram-mole	(obs. at 265-426°)

The calculated and observed heats of isomerization for the mixture of n-butenes are not in good agreement, probably because of the 240-400° discrepancy in temperature imposed by limited calorimetric data on the individual isomers. The calculated exothermic heats of isomerization of butene-1, *cis*-butene-2, and *trans*-butene-2 into isobutene are practically identical with the accepted 25° values: 3.580, 1.810, and 0.860 kilocalories per gram-mole, respectively.[581b, 586a] Other workers [529a] assume that the ratio of isobutene to n-butenes is about 0.57 for equilibrium conditions at 400°. This value should be less than 0.50 if the parameters 304 and 0.528 of the foregoing equation [199, 540] are correct.

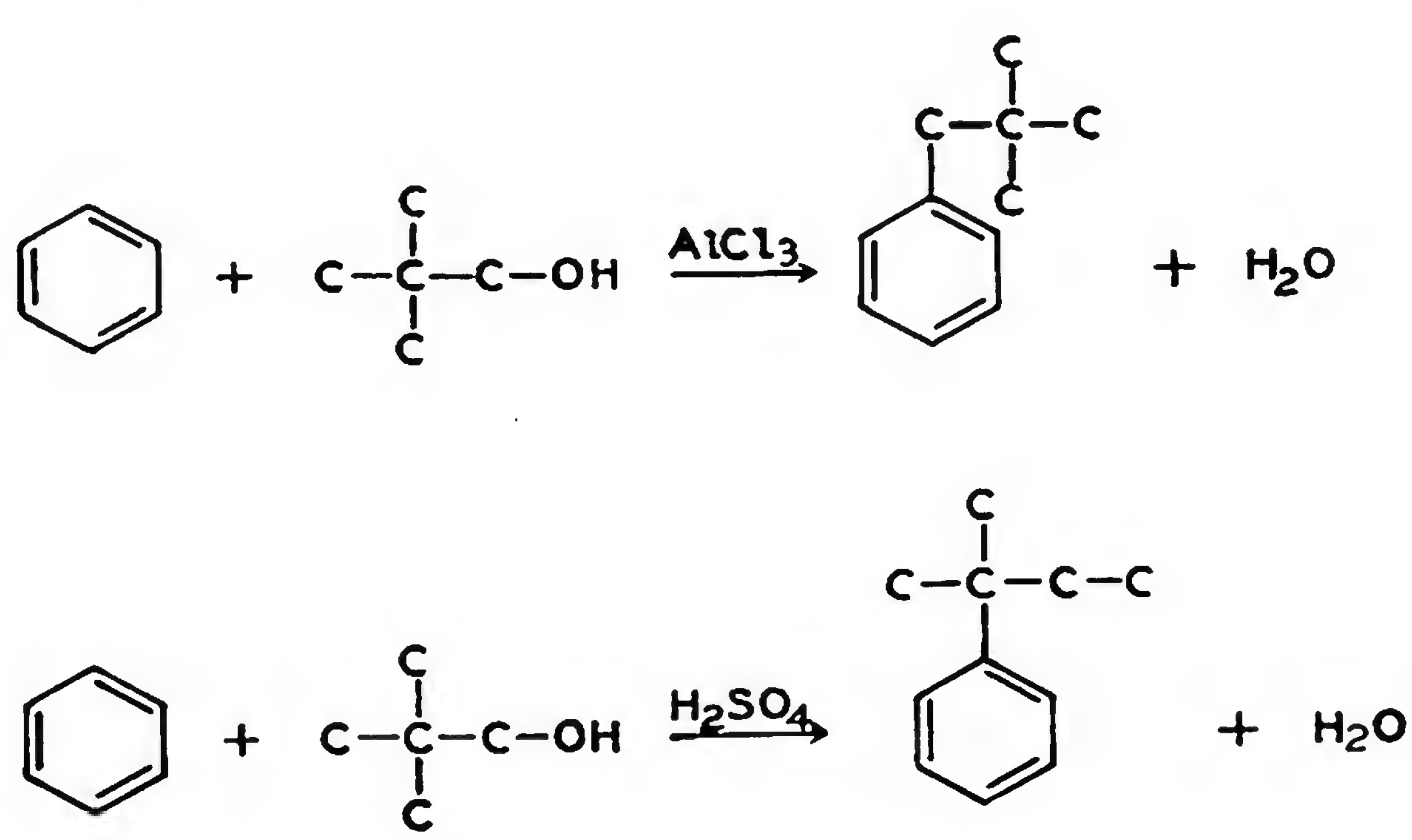
The isomerization of n-butenes into isobutene has been studied also in the presence of activated silica-aluminum at 385-600° with variable space velocities.[158] A 5.7-fold increase in space velocity at 600° changed the yield of isobutene only slightly (14.2 raised to 17.1 per cent), but decreased the side reactions so that the recovered n-butenes were 50.7 instead of approximately 36.8 per cent by weight of charged n-butenes.

Pentenes. A partial interconversion of pentene-1 and pentene-2 at 550-600° apparently takes place without formation of branched-chain pentenes or of cyclopentane.[261, 265] The last hydrocarbon has been considered a possible isomer.[497]

$$C{=}C{-}C{-}C{-}C \rightleftarrows C{-}C{=}C{-}C{-}C$$

Pentene-1 yielded a mixture of 21.7 per cent of pentene-1 and 78.3 per cent of pentene-2 when repeatedly passed over activated alumina at 357°.[172a] Passage of pentene-1 at 400° over an activated silica-alumina catalyst gave 59 per cent by weight of 2-methylbutenes among other products.[158] A catalyst comprising silica, alumina, and thoria in the proportions 100:5:0.5 is recommended.[581a] *n*-Pentenes passed over calcined alumina at 450° form 2-methylbutenes.[33] Sodium permutite can be used for the same purpose at 400° and 450°.[257a]

Isomerization has been found to accompany the alkylation of benzene with pentene-1 in the presence of sulfuric acid at 5°.[287] The normal product, 2-phenylpentane, was obtained together with 3-phenylpentane, indicating an isomerization.* Isomerization in alkylation may interfere with synthesis of hydrocarbons.[286] When such isomerization occurs, sulfuric acid leads to a more fundamental change in the structure than aluminum chloride.[287] Neopentyl alcohol, for example, reacts with benzene to give neopentylbenzene in the presence of aluminum chloride, whereas sulfuric acid, as catalyst, gives *tert*-amylbenzene.[442] In the first case there is apparently a simple dehydration, but in the second reaction an isomerization occurs as well. Isomerization of hydrocarbons in an alkylation by alcohols apparently involves either the *rearrangement of an intermediary alkene prior to the alkylation,* or *isomerization of the primary dehydration product* formed by condensation between alcohol and hydrocarbon through direct loss of water.

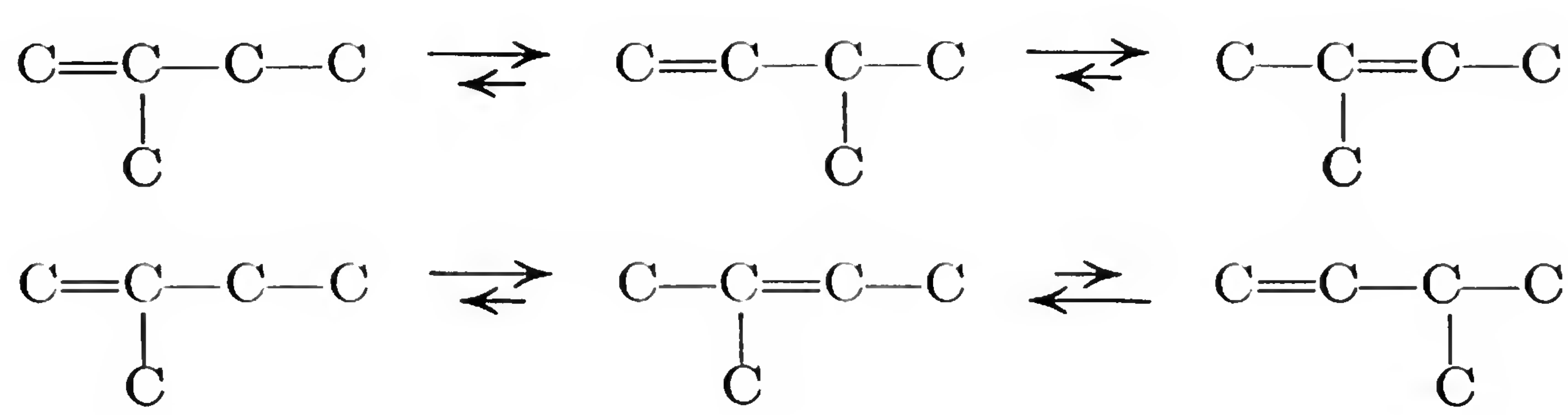


* The explanation of isomerization during alkylation in this and other examples remains incomplete to date. Further investigations of alkylation with various agents and of such competitive mechanisms as isomerizations of initial alcohols and of intermediate alkyl halides, esters, and alkenes are indispensable.

Pentene-2, heated at 600° in a carbonized silica tube, yielded decomposition products (carbon, methane, ethylene, propene, butene, butadiene-1-3, and hexene) but did not give branched-chain pentenes; only 33 per cent of pentene-2 was recovered.[413] The *cis* and *trans* forms of pentene-2 have been taken erroneously as electromeric forms[98, 301, 302, 356, 357, 544, 545]* *Cis*-pentene-2 has been isomerized to *trans*-pentene-2 by heating at 90-100° in the presence of xylene,[301] by combined heating (70-80°) and long exposure to sunlight,[545] and by exposure to ultraviolet light.[545] It is quite possible that all three of these effects were purely thermal. However, solvents may have a small effect upon the isomerization. *Cis*-pentene apparently undergoes a slight transformation into the *trans* form when dissolved in acetic acid.[98] *Trans*-pentene-2 is converted partly into *cis*-pentene-2 upon exposure to ultraviolet light[544] or upon dissolution in acetic acid.[98] Certain early experiments on the isomerization of pentene-2 are inconclusive.[609aa]

Pentene-2 has been isomerized slightly to pentene-1 by prolonged catalysis over activated alumina at 266-364°, alumina plus cobaltous oxide at 320° and 375°, alumina plus chromic oxide at 295° and 345°, alumina plus ferric oxide at 295° and 344°, or alumina plus manganous oxide at 301-366°.[172a] The yields of pentene-1 and pentene-2 at 364° averaged 15.3 and 84.7 per cent, respectively, which are probably the equilibrium values.

2-Methylbutene-1 was isomerized to an equilibrium mixture containing 27.0, 3.6, and 69.4 per cent of 2-methylbutene-1, 3-methylbutene-1, and 2-methylbutene-2, respectively, by a prolonged recirculation over activated alumina at 357°.[172a] Products of practically the same composition as the foregoing mixture were obtained by similar treatments of 3-methylbutene-1 at 362° and of 2-methylbutene-2 at 356°. *n*-Pentenes were absent in these isomerizates. Reaction rate studies would enable a decision to be made concerning the following theoretical mechanisms for the foregoing isomerizations:



Probable values of the equilibrium mixture compositions and corresponding equilibrium constants for branched pentenes, calculated from

* Physical constants of *cis*- and *trans*-pentene-2[154] have been found of considerable value in distinguishing the recorded "electromeric," "isomeric," "lower-boiling," "higher-boiling," "labile," and "stable" forms.

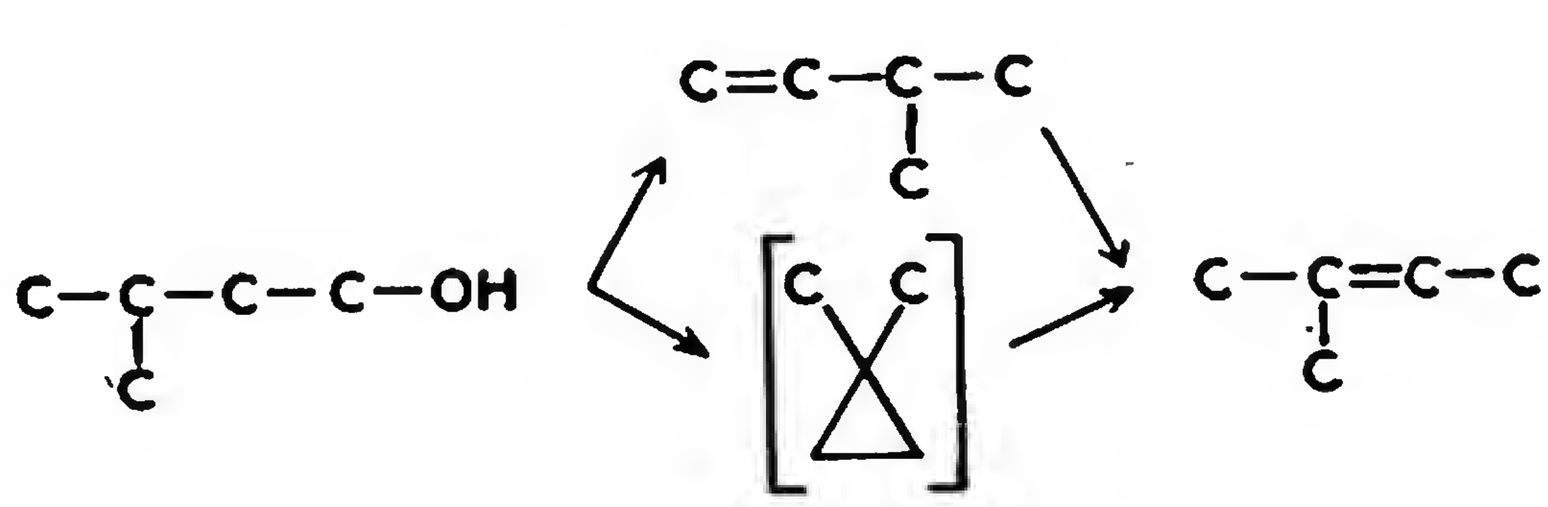
data[172a] mainly on isomerization of 2-methylbutene-2, are given in the following compilation:

Temp. (°C.)	Equilibrium Concentrations, weight per cent: C=C(C)—C—C	C=C—C(C)—C	C—C(C)=C—C	Probable Equilibrium Constants: $K_1 = \frac{\text{C—C(C)=C—C}}{\text{C=C(C)—C—C}}$	$K_2 = \frac{\text{C—C(C)=C—C}}{\text{C=C—C(C)—C}}$	$K_3 = \frac{\text{C=C(C)—C—C}}{\text{C=C—C(C)—C}}$
251	22.6	1.8	75.6	3.35	42.0	12.6
300	25.6	2.5	71.9	2.81	28.8	10.2
358	27.3	3.5	69.2	2.53	19.8	7.8
400	28.2	5.0	66.8	2.37	13.4	5.6

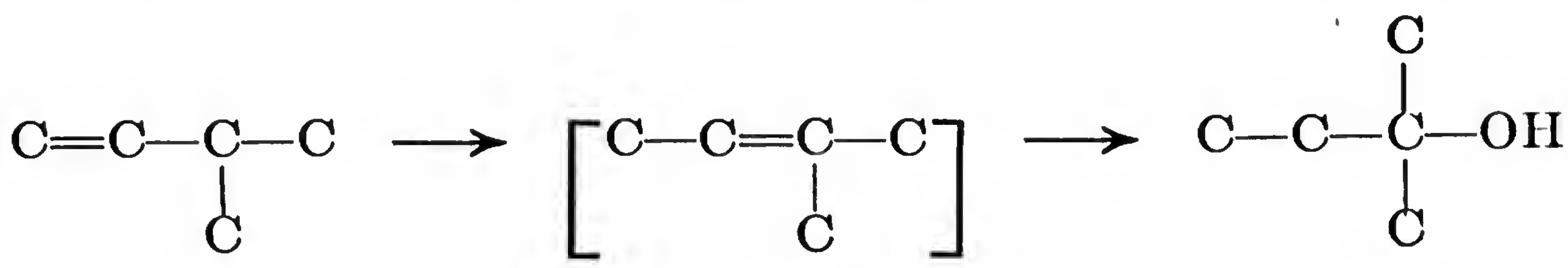
These data indicate that the concentration of 3-methylbutene-1 is doubled by a 100° increase in temperature. The heats of hydrogenation of 2-methylbutene-1, 3-methylbutene-1, and 2-methylbutene-2 at 82° are 28.491 ± 0.10, 30.336 ± 0.06, and 26.920 ± 0.06 kilocalories per gram-mole of vapor, respectively.[140a, 305] Appropriate subtraction of these heat quantities gives 1.571 ± 0.12, 3.416 ± 0.08, and 1.845 ± 0.12 kilocalories per gram-mole of vapor at 82° as the exothermic heats of isomerization corresponding to equilibria K_1, K_2, and K_3.

Isomerization of 3-methylbutene-1 into 2-methylbutene-2 (55-80 per cent) in the presence of alumina at 450-560° was reported to occur irreversibly.[271] Alumina at 450°, aluminum sulfate at 425°, and phosphoric acid on pumice at 500°, as catalysts in the isomerization of 3-methylbutene-1, gave 10, 47, and 29 per cent yields of 2-methylbutene-2, respectively.[413] These isomerizations also were found to be irreversible.

In isomerization of 3-methylbutene-1 to 2-methylbutene-2 by heating the pure hydrocarbon or during the dehydration of isoamyl alcohol, the relative effectiveness of alumina and aluminum sulfate as catalysts is always the same. The conversion into 2-methylbutene-2 is greater when the alcohol is dehydrated. Isoamyl alcohol and alumina at 450° gave an "amylene" containing 90 per cent of 3-methylbutene-1, but isoamyl alcohol and aluminum sulfate at 345° formed an "amylene" having about 79 per cent of 2-methylbutene-2.[413] In the dehydration giving 2-methylbutene-2, 1,1-dimethylcyclopropane may be an intermediate product:

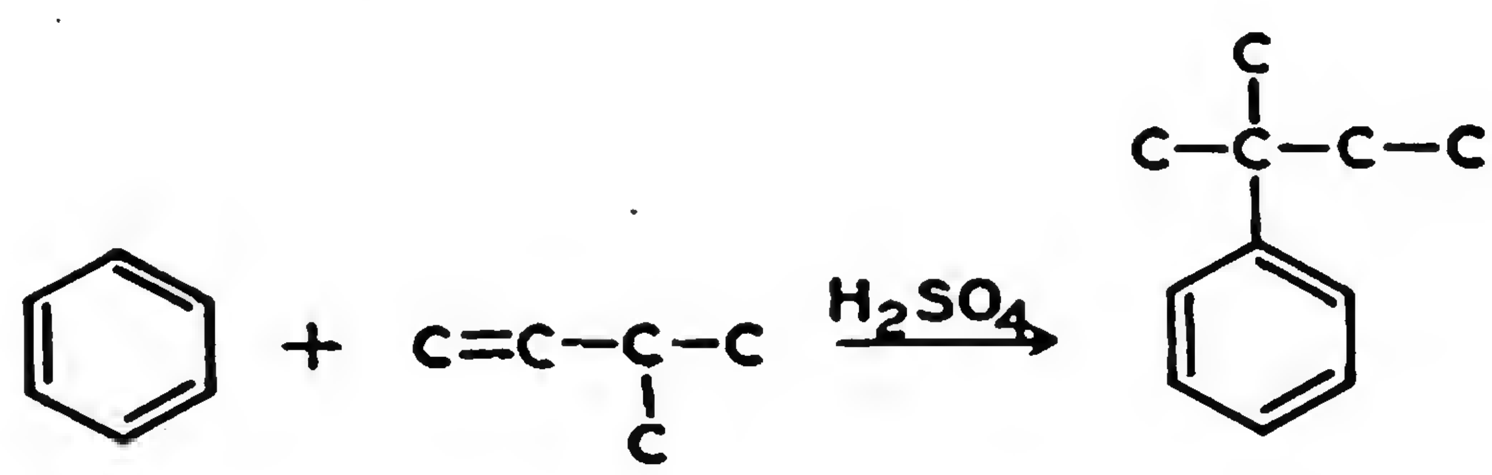


The action of 60-per cent sulfuric acid on 3-methylbutene-1 for one hour at 38° gave a polymer and a solution from which *tert*-amyl alcohol was recovered.[413] The formation of *tert*-amyl alcohol may involve an intermediary isomerization of 3-methylbutene-1 into 2-methylbutene-2:

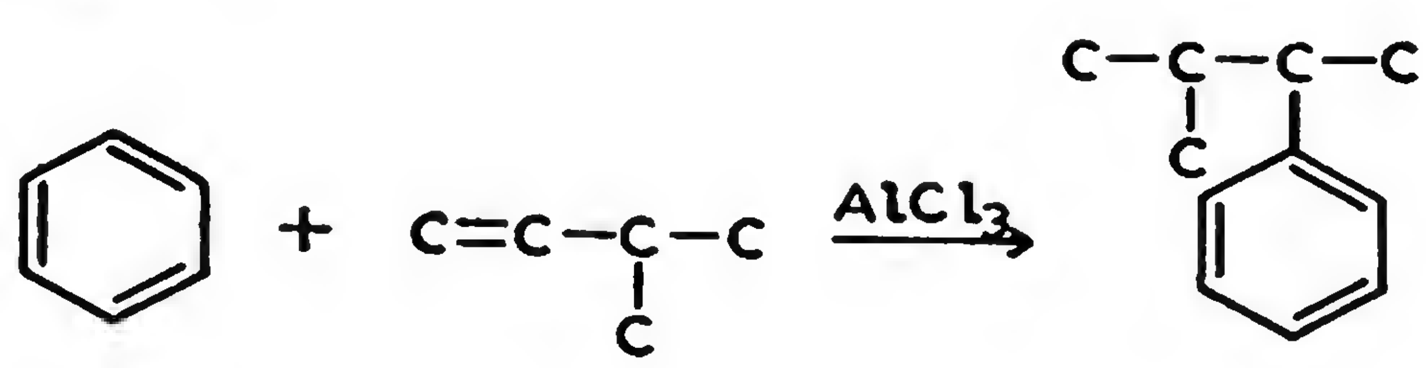


At the slightly lower temperature of 30-35°, 3-methylbutene-1 is stable toward 60-per cent sulfuric acid. An isomerization into 2-methylbutene-2 can take place, though only to a slight extent, by the use of an acid of such concentration that polymerization does not occur appreciably.[413]

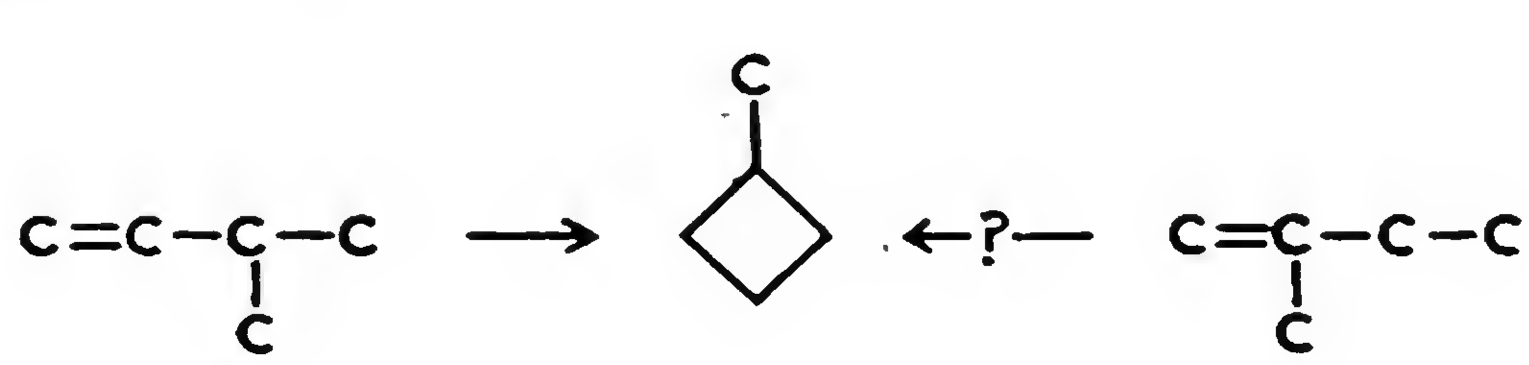
The isomerization of 3-methylbutene-1 into 2-methylbutene-2 may occur also in the alkylation of benzene to *tert*-amylbenzene by 3-methylbutene-1 in the presence of 96-per cent sulfuric acid at 0°:[286]



However, aluminum chloride at 4-6°. leads to the normal product, 2-methyl-3-phenylbutane:[287]



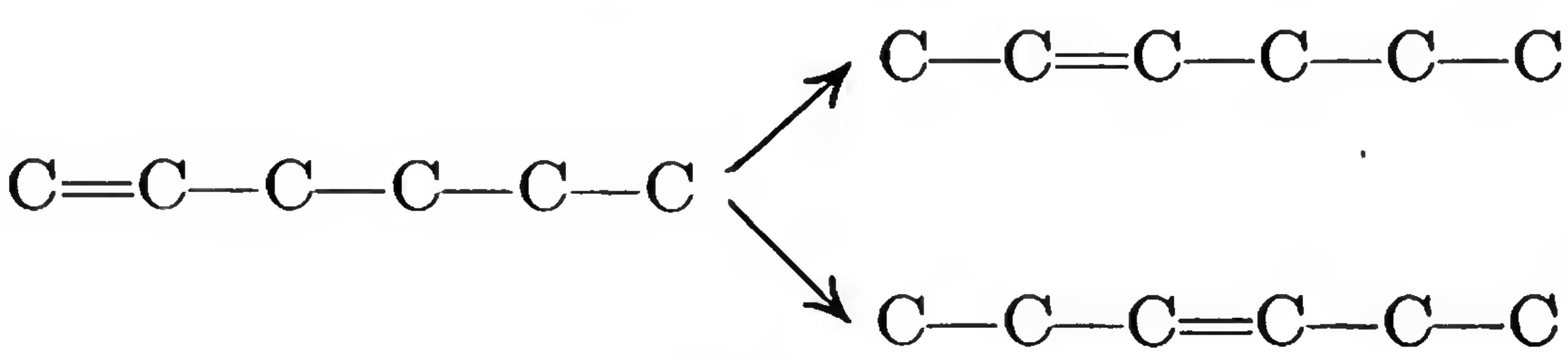
Amylene boiling up to 42° C. (impure!), prepared according to Würtz[657] and Eltekov,[163] was isomerized by treatment with 50 per cent of aluminum chloride for 5 weeks at 0-20°.[16] The reaction was given as a cyclization of 3-methylbutene-1 into methylcyclobutane and formation of heavier cyclanes and alkanes. A cyclization of 2-methylbutene-1, which is a possible component of the amylene, could have occurred, but has never been considered or verified:



A small amount of work has been conducted on the equilibrium between 2-methylbutene-2 and *n*-pentenes at 400° in the presence of a permutite catalyst.[529a] The equilibrium product has 80 per cent of 2-methylbutenes, after correcting for side products amounting to 15 per cent.

Hexenes. Hexene-1, heated one hour at 400° under 40(?) atmospheres' initial pressure of hydrogen in the presence of 5 per cent of molybdenum trisulfide, formed a significant amount of hexene-2 and some

hexene-3, indicating that isomerization occurs by a shifting of the double bond.[437] Hexenes of iso-structure were not isolated, neither was there any change in hexene-1 heated with molybdenum trisulfide for one hour at 300°. Hardly any side products boiling lower than hexene-1 were formed at 400°, in contrast with heptane and octane treated under the same conditions, but polymerization began at 350° and was considerable at 400°.



Thermodynamic data [497, 651] predict that hexene-1 should form cyclohexane and methylcyclopentane, but these products have not been reported.

n-Hexenes form 3-methylpentene-2 and/or 2-ethylbutene-1 when passed over alumina at 400°, according to an old patent.[33] Recently, hexene-1 was passed over alumina at 398° at varying rates, as well as over thoria.[220] The products* included isomers, such as hexene-2, hexene-3, 2-methylpentene-2, 3-methylpentene-2, and 2-ethylbutene-1, some of which were again passed over the catalysts under comparable conditions; the results are presented in Table 8. These investigators formulated the following conclusions on isomerization of hexenes:

Table 8. Isomerization of Hexenes as Related to Their Structure, Reaction Conditions and Products [220]

Reactants		Conditions		Percentage Composition of Products									
Hexene	Catalyst	cc. Hexene feed per hour per 10 g. catalyst	Temp. (°C.)	Hexene-1	Hexene-2	Hexene-3	2-Methyl-pentene-1	2-Methyl-pentene-2	Lower-boiling 3-Methyl-pentene-2	Higher-boiling 3-Methyl-pentene-2	2-Ethyl-butene-1	Isohexane	Polymers
Hexene-1	Al_2O_3	3.1	398	5.9	..	11.3	..	27.7	9.8	5.3	38.7	..	.
Hexene-1	Al_2O_3	11.2	398	24	2	8	..	12	36	5	13	..	.
Hexene-1	Al_2O_3	22.5	398	89	..	..	..	..	9.2	..	1.8	..	.
Hexene-1	Al_2O_3	45.5	398	92	..	..	..	..	8	..	..	..	.
Hexene-1	ThO_2	3.12	398	..	..	..	..	..	90	..	5	..	5
2-Methylpentene-2	Al_2O_3	3.12	398	..	..	..	..	62	35	..	..	..	3
2-Methylpentene-2	ThO_2	3.12	398	..	..	..	..	2	70	..	25	..	3
Lower-boiling 3-methylpentene-2	Al_2O_3	3.12	398	..	..	..	..	22	70	..	5	..	3
Lower-boiling 3-methylpentene-2	Al_2O_3	3.12	440	..	..	..	29	8	52	..	6	2	3
Lower-boiling 3-methylpentene-2	ThO_2	3.12	398	..	..	..	..	7	70	..	19	..	4
Lower-boiling 3-methylpentene-2	ThO_2	3.12	440	..	..	..	16	5	40	..	30	3	6
2-Ethylbutene-1	ThO_2	3.12	398	..	..	..	..	2	69	..	26	..	3

* Recent work [473, 612] on the separation of isomeric hexenes by fractional distillation sharply contradicts the reported "facile" separation of these isomerization products.

1. The straight-chain hexene is the least stable at 400°.

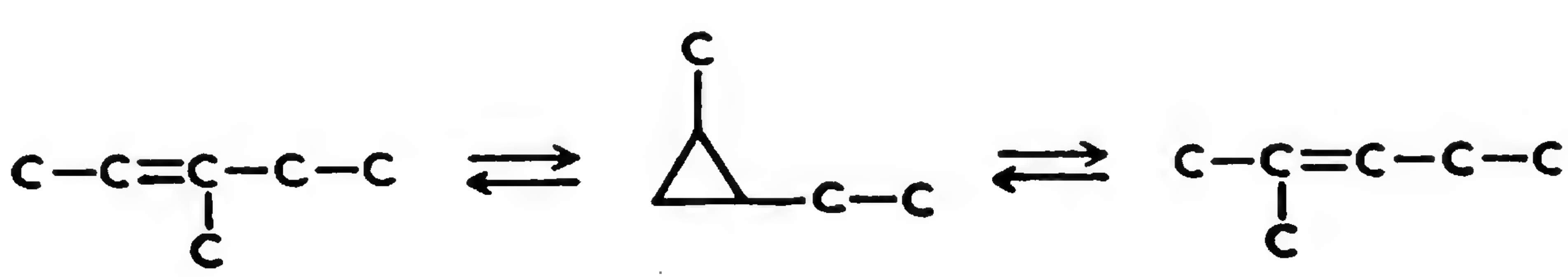
2. The 2-methylpentenes give the corresponding 3-methylpentenes in large quantities.

3. The 2-ethylbutene-1 is the result of double-bond migration.

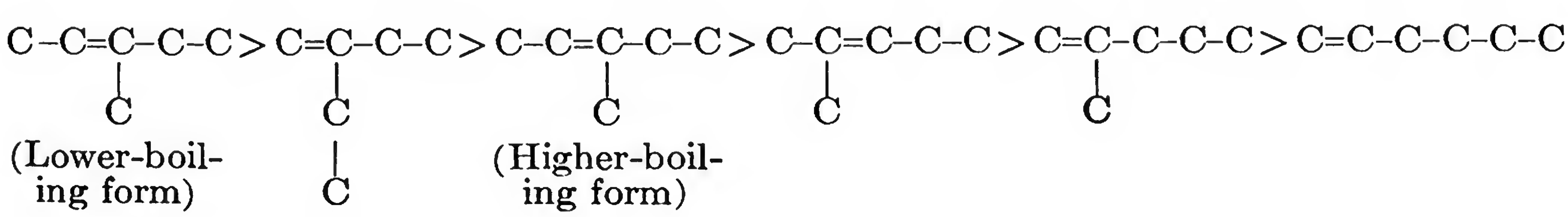
4. 2-Ethylbutene-1 passed over thoria gives the same product as that obtained from the 2- and 3-methylpentenes.

5. Increase in temperature to 440° causes the shift of the double bond to the end of the chain and the formation of 2-methylpentene-1. Isohexane is formed simultaneously as a result of dehydrogenation-hydrogenation.

6. The products are in agreement with the hypothesis of an activated-intermediate stage, actually a cyclization of hexenes into unstable substituted cyclopropanes, *e.g.*,



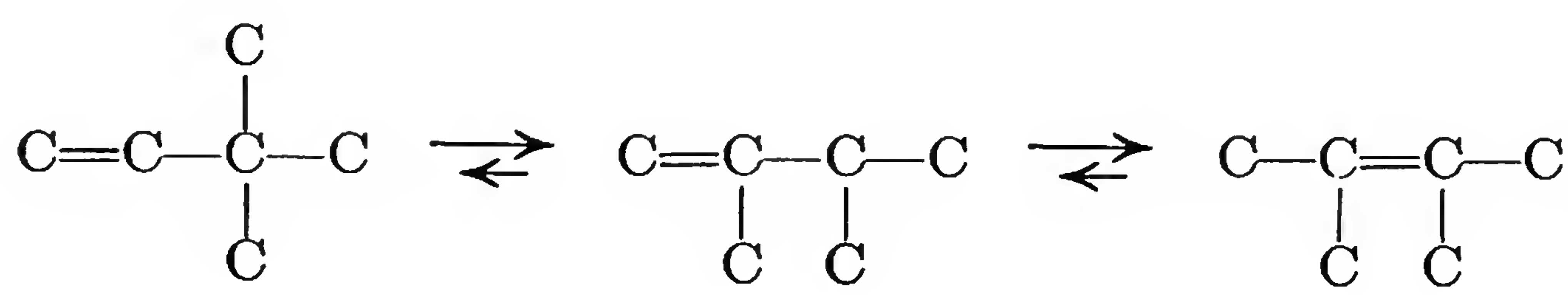
7. The order of stability at 400° was found to be as follows:



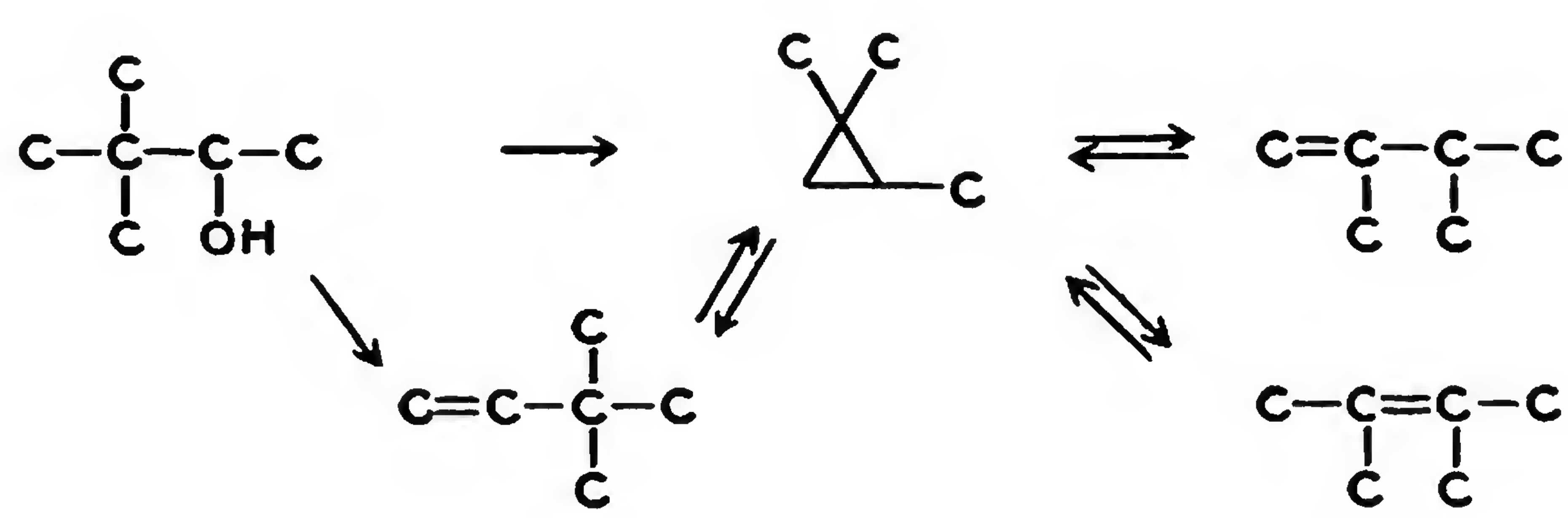
The catalytic action of zinc chloride on pumice (1:1) upon hexene-1 was studied for the purpose of finding out whether an isomerization would occur with the change of carbon-chain configuration.[436] The amount of isomers (23 per cent) was determined by hydrogenating the product and then determining the tertiary carbon-atom content by the antimony pentachloride method. The reaction took place in 1.5 hours at 300-325° and 50 atmospheres' initial pressure of nitrogen, with formation of over 15 per cent of high-boiling side products. Hexene-1, heated 4-5 hours at 325-350° with phosphoric acid on pumice (1:1) under 60 atmospheres' pressure, gave approximately 15 per cent of 2-methylpentene-2.[438]

Treatment of 3,3-dimethylbutene (*tert*-butylethylene) with phosphorus pentoxide on silica gel at 300° gave 15 per cent of 2,3-dimethylbutene-1, 30 per cent of 2,3-dimethylbutene-2, together with traces of 3,3-dimethylbutene and a considerable amount of a polymerized product.[329] A similar contact with sodium permutite at 310° showed almost complete conversion into 2,3-dimethylbutenes-1 and -2.[267a, 529a] Activated alumina at 350° is without action on 3,3-dimethylbutene, but anhydrous aluminum sulfate at 275° gives 29.7 per cent of 2,3-dimethylbutene-1,

55.5 per cent of 2,3-dimethylbutene-2, together with 3.8 per cent of 3,3-dimethylbutene.[130] Individual treatments [329] of 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2 with phosphorus pentoxide on silica gel at 300° gave quantitatively the same products as did 3,3-dimethylbutene. In a previous investigation,[643] the dehydration of pinacolyl alcohol over phosphorus pentoxide on silica gel at 300° gave isomeric hexenes in the proportions: 3,3-dimethylbutene (3 parts), 2,3-dimethylbutene-1 (31 parts), and 2,3-dimethylbutene-2 (61 parts). From these facts, it was concluded that an equilibrium state exists among these hexenes. This equilibrium, including reaction displacements, can be formulated as follows:



As an alternative explanation to the foregoing equilibria, the dehydration of pinacolyl alcohol and the interconversions of 3,3-dimethylbutene, 2,3-dimethylbutene-1, and 2,3-dimethylbutene-2 may be considered as due to an intermediary formation of 1,1,2-trimethylcyclopropane:



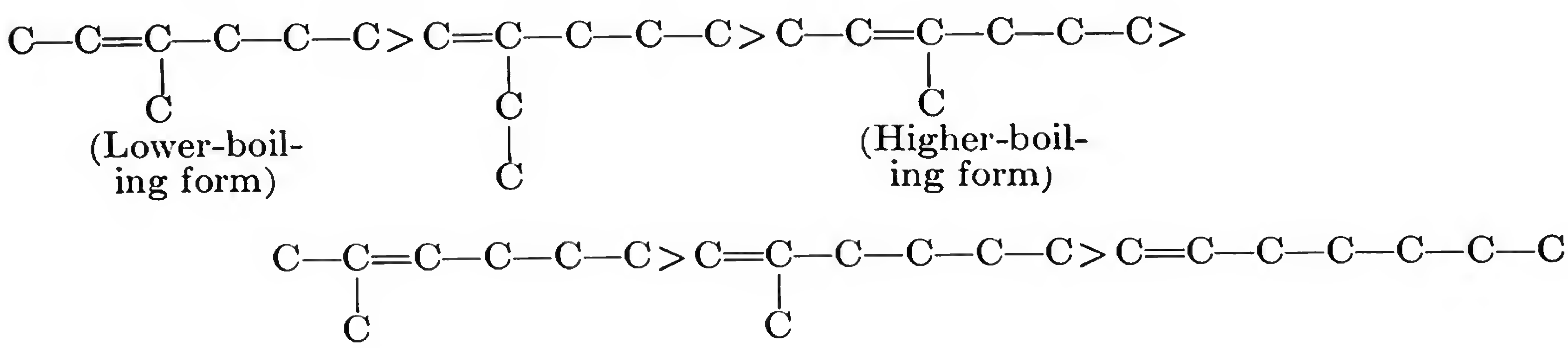
An older mechanism proposed for the interconversion of these hexenes is the addition of a proton from the catalyst to one of the carbon atoms of a double bond, leaving the other carbon atom temporarily with only six electrons:[329]

$$H_2C::\underset{\underset{H}{\cdot\cdot}}{C}:\overset{\overset{CH_3}{\cdot\cdot}}{\underset{\underset{CH_3}{\cdot\cdot}}{C}}:CH_3 + H^+ \rightleftarrows H_2C:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{\overset{+}{C}}}:\overset{\overset{CH_3}{\cdot\cdot}}{\underset{\underset{CH_3}{\cdot\cdot}}{C}}:CH_3 \rightleftarrows H_3C:\underset{\underset{H_3C}{\cdot\cdot}}{C}::\underset{\underset{CH_3}{\cdot\cdot}}{C}:CH_3 + H^+$$

This general mechanism is objected to by several investigators [38, 93, 425] because it involves positive carbonium ions. A modern and more "complete" mechanism should consider resonance energy and solvent effects, partial valences, and activated-complex formation.[635]

Heptenes. The isomerization of heptenes has been studied mainly by two investigators.[220] Heptene-1, passed over alumina at 398°, gave 70 per cent of 3-methylhexene-2 and 5 per cent of 2-ethylpentene-1. Pas-

sage of 2-methylhexene-2 at 398° over alumina or thoria resulted respectively in 40 and 72 per cent of 3-methylhexene-2, along with 15 and 20 per cent of 2-ethylpentene-1. The treatment of 3-methylhexene-2 at 398° with thoria or alumina gave respectively 2 and 10 per cent of 2-methylhexene-2, together with 15 and 2 per cent of 2-ethylpentene-1. Increase of temperature to 440° in the last two cases resulted in the formation of 11 and 18 per cent of 2-methylhexene-1, and 7 and 4 per cent of isohexane. Passage of 2-ethylpentene-1 over thoria at 398° yielded 3 per cent of 2-methylhexene-2 and 71 per cent of 3-methylhexene-2. The isomerizations of these heptenes are compared in Table 9. The conclusions to be gathered from this table are analogous to those given for isomerization of hexenes under identical conditions. The following order of stability of heptenes at 400° was given:



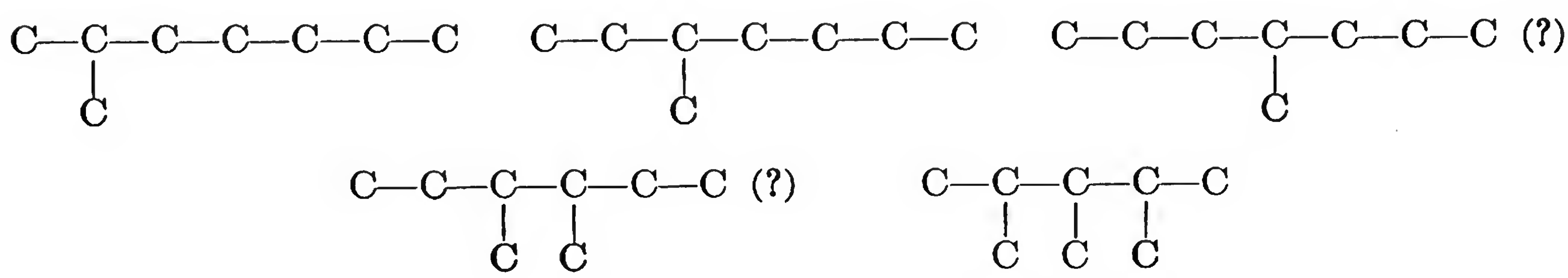
Heptene-1 (b.p. 91.9-92.0°/741 mm. Hg, $D^{20}_{4}=0.6974$, $n^{20}_{D}=1.4000$) probably formed a small amount of 3-methylhexene-2 when passed slowly over beryllium oxide at 450°.[12a] The main fraction (b.p. 92-95°, n^{20}_{D}

Table 9. Isomerization of Heptenes as Related to their Structure, Reaction Conditions and Products.[220]

Reactants: Heptene	Catalyst	Conditions: cc. Heptene feed per hour per 10 g. catalyst	Temp. (°C.)	Percentage Composition of Products: Heptene-1	2-Methylhexene-1	2-Methylhexene-2	3-Methylhexene-2	2-Ethylpentene-1	Isohexane	Polymers
Heptene-1	Al_2O_3	3.12	398	25	..	..	70	5	..	..
2-Methylhexene-2	Al_2O_3	3.12	398	..	..	42	40	15	..	5
2-Methylhexene-2	ThO_2	3.12	398	..	..	3	72	20	..	5
3-Methylhexene-2	Al_2O_3	3.12	398	..	..	10	82	2	..	6
3-Methylhexene-2	Al_2O_3	3.12	440	..	18	5	63	3	4	7
3-Methylhexene-2	ThO_2	3.12	398	..	..	2	76	15	..	7
3-Methylhexene-2	ThO_2	3.12	440	..	11	8	45	20	7	9
2-Ethylpentene-1	ThO_2	3.12	398	..	..	3	71	21	..	5

$=1.4074$) of the once-through product was re-treated to form a richer condensate (b.p. 92-96°, $D^{20}_{4}=0.7041$, $n^{20}_{D}=1.4082$). The latter was hydrogenated at 140° in the presence of platinized charcoal, yielding a n-heptane and 3-methylhexane mixture (b.p. 92.0-96.0°/749 mm. Hg, $D^{20}_{4}=0.6836$, $n^{20}_{D}=1.3889$).

Octenes. Heating a mixture of octene-1 and octene-2 at 295-365° in quartz tubes gave a low-boiling product, corresponding to one per cent of isoöctenes and "practically" no gases.[259] Zinc chloride, zinc chloride on pumice (1:1), and phosphoric acid on pumice (1:1) catalyzed the isomerization of an octene-1 and octene-2 mixture to "iso-products" accompanied by low- and high-boiling side products.[436] These processes all required large amounts of "catalyst"; they gave a higher degree of isomerization in a shorter time when under nitrogen pressure. The mixed octene-1 and octene-2 heated in the presence of zinc chloride at 325-350° for 25 hours under atmospheric pressure, or for 1.5 hours at 300-325° under 50 atmospheres' initial pressure of nitrogen, yielded respectively 12 and 46.8 per cent of iso-compounds upon hydrogenation.[436] An activated silica-alumina mass converted a mixture of octene-1 and octene-2 (prepared by the dehydration of octanol-2) into 58.2 and 60.5 per cent by weight of branched-chain octenes at 375° and 385°, respectively, prior to active cracking.[158] The products (branched-chain octenes) were next hydrogenated in the presence of a nickel catalyst, giving the following alkanes:

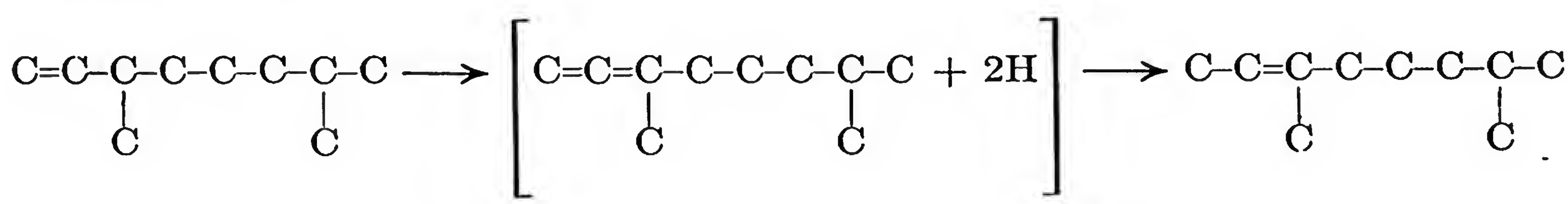


Hence, the isomerization of the mixture of octene-1 and octene-2 gave the following isomers*: 2-methylheptene-x, 3-methylheptene-x and/or 2-ethylhexene-1; 4-methylheptene-x and/or 2-propylpentene-1; 3,4-dimethylhexene-x and/or 2-ethyl-3-methylpentene-1; 2,3,4-trimethylpentene-x and/or 2-isopropyl-3-methylbutene-1. It was stated that following the initial isomerization there occurs a catalytic decomposition into propene, butenes, and pentenes. Therefore, it appears that the primary reaction is chiefly isomerization, and that decomposition essentially follows the isomerization. Both primary and secondary reactions apparently involve C—C ruptures, but differ in their extent and mode of recombination. The conclusion "cracking for the most part followed isomerization" of octenes[158] is based upon the presence of about equal proportions of n-butenes as compared to isobutene in gases accompanying the reaction, and upon an observed much slower isomerization of n-butenes into isobutene over the catalyst at a corresponding rate of flow. Other experimenters[397] claim that thermal treatment of octene-1 and octene-2 at 345-380° leads to polymers and that increased

* Tentatively, since the locations of double bonds are still unknown.

thermal effect and reaction duration gives isoöctenes due to depolymerization. The last experiments are difficult to interpret, because of an 8.3 per cent content of isoöctenes in the material charged, as determined by the antimony pentachloride method. A catalyst comprising silica, alumina, and thoria in the proportions 100:5:0.5 is recommended for the isomerization of *n*-octenes into branched octenes.[581a] Sodium permutite has also been used for this purpose.[257a, 417a, 421a] Phosphoric acid can effect a conversion of 2,4,4-trimethylpentenes-1 and -2 into a 2,3,4-trimethylpentene, but the details of these isomerizations are lacking.[561a]

Decenes. An exceptionally complete isomerization of 3,7-dimethyloctene-1 into 3,7-dimethyloctene-2, by double-bond shifting, occurred upon passage over a palladium-asbestos catalyst at 200° in a stream of carbon dioxide.[670] Formation of an allene intermediate was proposed:



Hexadecene. Passage of cetene over an activated silica-alumina catalyst at 300°, 350°, 400°, and 450° gave 8.0, 44.9, 26.9, and 13.0 per cent by weight, respectively, of lower-boiling hexadecenes, assumed to have branched-chain structure.[158] It was postulated that following the initial isomerization, a decomposition to numerous smaller hydrocarbons occurs.

The experimental data on the isomerization of alkenes in the presence of various catalysts are presented in Table 10, p. 244.

Conclusions

1. An isomerization of alkenes unaccompanied by the formation of side products, proceeds by an apparent shifting of the hydrogen atom, resulting in change of double-bond position or in *cis-trans* isomerization.

2. A more extensive transformation with change in carbon-chain configuration takes place under more severe conditions (higher temperature, stronger catalyst). This involves two consecutive reactions: loosening of the C—C bond in the presence of the catalyst (dealkylation or "depolymerization") and recombination (such as alkylation by radicals and alkenes; or polymerization). Under these conditions cyclization can occur also.

3. Side products, *i.e,* smaller and larger molecules, accompany an isomerization with chain branching, because of the ease with which the branched alkenes can be polymerized and depolymerized.

Alkadienes

The unsaturated aliphatic hydrocarbons containing two double bonds are highly reactive. They readily undergo hydrogen-atom migration by shifting of double bonds, cyclization, or polymerization. Because of differences in structure and mechanism, the members of this group are considered separately as allenic and non-allenic alkadienes.

Allenic Alkadienes

The thermal isomerizations of alkadienes apparently involve "detachment" of hydrogen:

$$H_2C{=}C{=}CH_2 \rightleftarrows \left[HC{\equiv}C{-}CH_2 + H\right] \rightleftarrows HC{\equiv}C{-}CH_3$$

$$\underset{\displaystyle CH_3}{H_2C{=}C{=}\overset{}{C}{-}CH_3} \rightleftarrows \left[\underset{\displaystyle CH_3}{H_2C{=}C{-}\overset{}{C}{=}CH_2} + H\right] \rightleftarrows \underset{\displaystyle H\quad CH_3}{H_2C{=}C{-}C{=}CH_2}$$

Propadiene (*i.e.*, allene), when passed over "Floridin" at 167-350°, yielded propyne (*i.e.*, allylene) and polymers.[552] Heated with ether and sodium at 100°, propadiene yielded the sodium derivative of propyne.[239] Propadiene, treated 12 hours at 160-170° with alcoholic potash,* gave propyne and ethyl isopropenyl ether (intermediate product), together with *unreacted propadiene*.[179] The mechanism of isomerization and the presence of propadiene in the product will be considered again under the Alkynes:

$$H_2C{=}C{=}CH_2 + C_2H_5OH \longrightarrow \underset{\displaystyle OC_2H_5}{H_2C{=}C{-}CH_3} \rightleftarrows HC{\equiv}C{-}CH_3 + C_2H_5OH$$

Butadiene-1,2 (*i.e.*, methylallene), in the presence of "Floridin" at 245-300°, isomerized to 3.4 per cent of butyne-1 and traces of butadiene-1,3.[549] Butadiene-1,2 heated with sodium and ether, or with alcoholic potash, gave a butene plus the sodium derivative of butyne-1, and free butyne-2, respectively.[292]

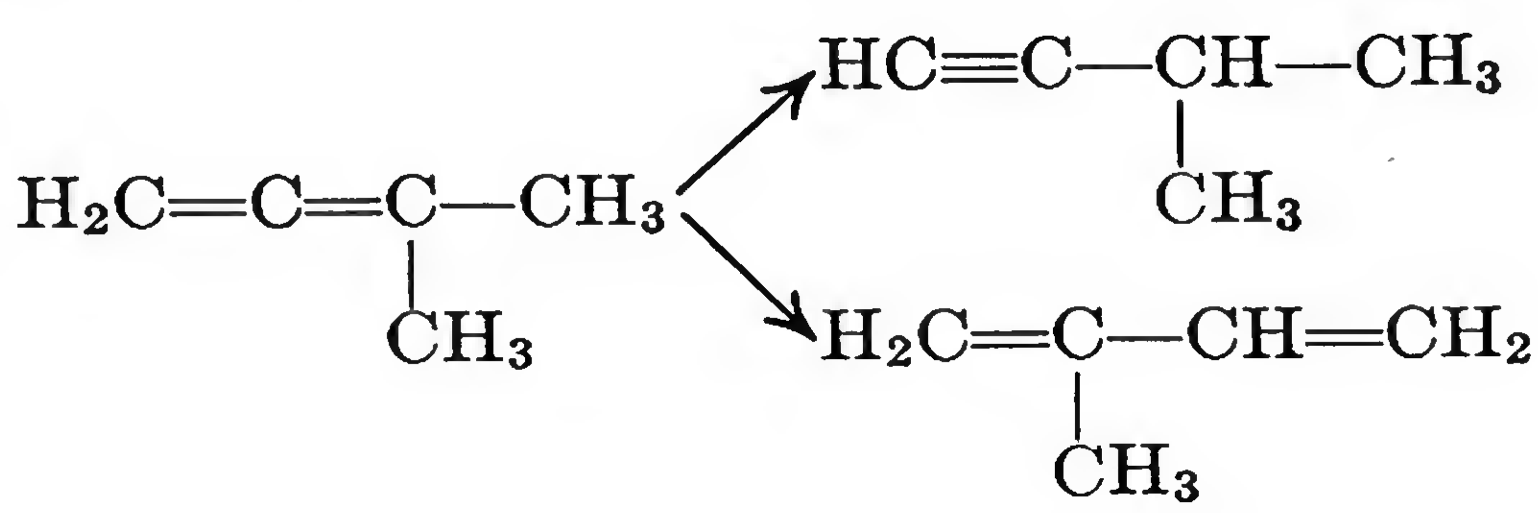
$$H_2C{=}C{=}CH{-}CH_3 \longrightarrow \begin{cases} H_2C{=}CH{-}CH{=}CH_2 \\ HC{\equiv}C{-}CH_2{-}CH_3 \\ H_3C{-}C{\equiv}C{-}CH_3 \end{cases}$$

* "Alcoholic potash" results when potassium hydroxide and anhydrous ethanol are mixed, forming potassium ethoxide and water. This reaction is reversible and is favored by heating of the mixture, but then some secondary reactions occur.[649] The resultant or even accidentally introduced water influences the isomerization to an unknown extent, so that it seems desirable to repeat some of the experiments in the presence of pure potassium ethoxide (devoid of ethanol and water).

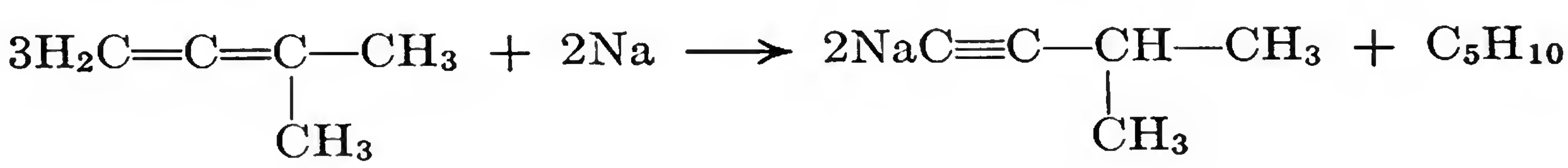
Pentadiene-1,2 (ethylallene) with xylene or petroleum of boiling point above 180°, treated 2 hours at 140° with a slight excess of sodamide (suspended in Vaseline), gave the sodium derivative of pentyne-1.[79] As the reaction mixture approached 100-120°, ammonia gas was liberated.

$$C{=}C{=}C{-}C{-}C \longrightarrow C{\equiv}C{-}C{-}C{-}C$$

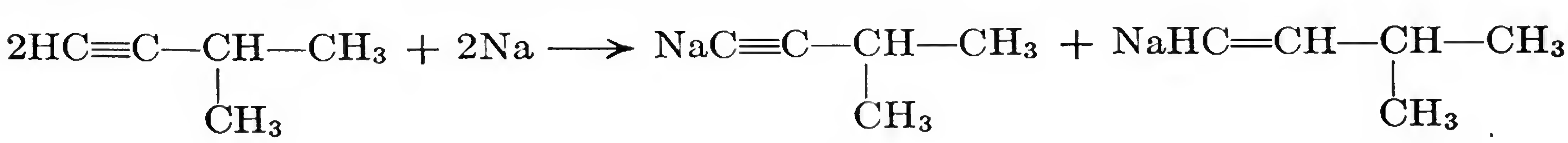
3-Methylbutadiene-1,2 (unsym-dimethylallene), at 215-334° in the presence of activated "Floridin," isomerized incompletely into 2-methylbutadiene-1,3 (isoprene) and 3-methylbutyne-1 (isopropylacetylene).[548] 3-Methylbutadiene-1,2, heated alone at 100-225° in sealed tubes, gave several types of polymers and a small amount of 2-methylbutadiene-1,3.[330] Alumina at 300° catalyzed an isomerization of 3-methylbutadiene-1,2 into 2-methylbutadiene-1,3.[31, 638]



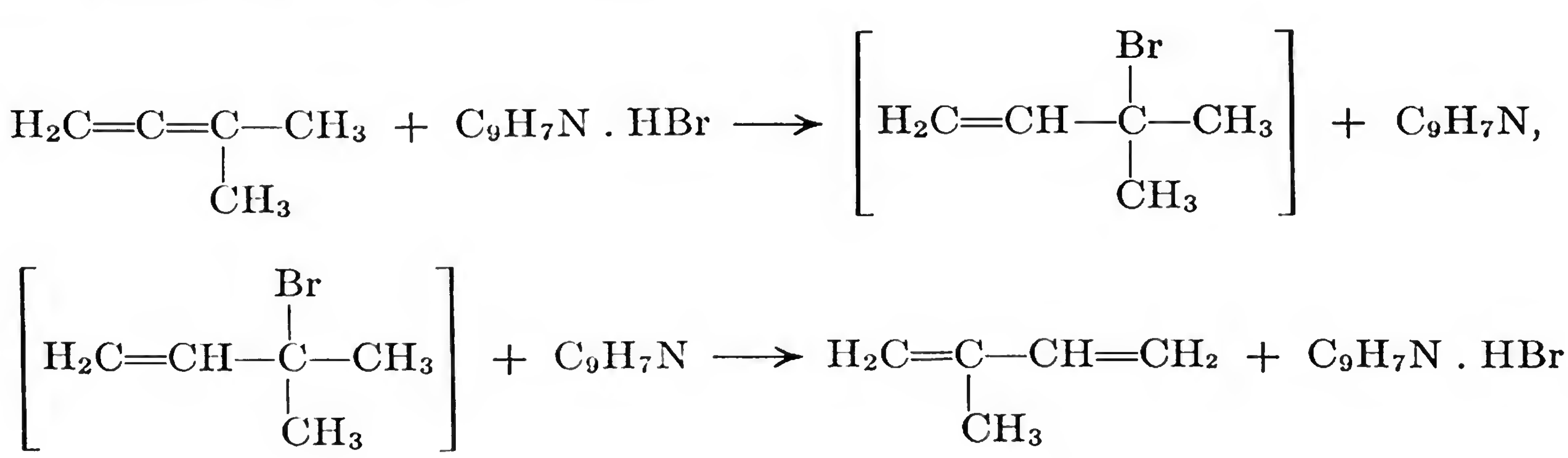
3-Methylbutadiene-1,2, heated with sodium at 100°, gave the sodium derivative of 3-methylbutyne-1, hydrolyzed by water to the alkyne.[176] The reaction was presumed to follow the equation,[177]

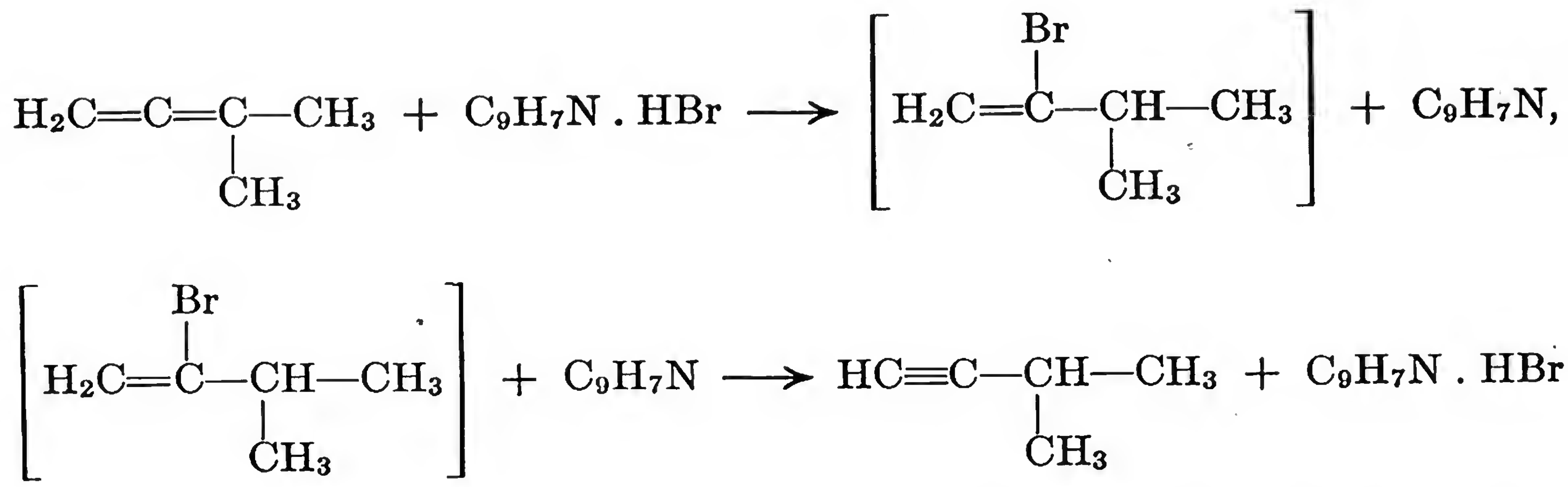


which is in disagreement with a previous explanation: [164]



Heating of 3-methylbutadiene-1,2 with quinoline hydrobromide resulted in the irreversible formation of 50-55 per cent of 2-methylbutadiene-1,3, together with some 3-methylbutyne-1.[326] The reaction mechanism proposed was as follows:

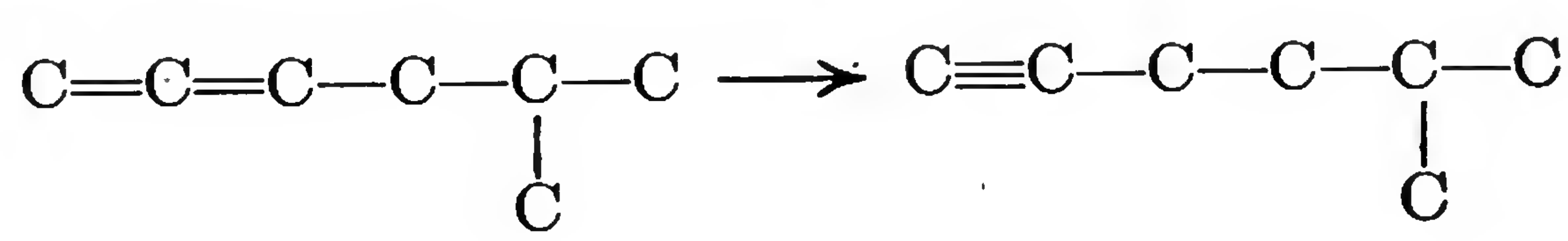




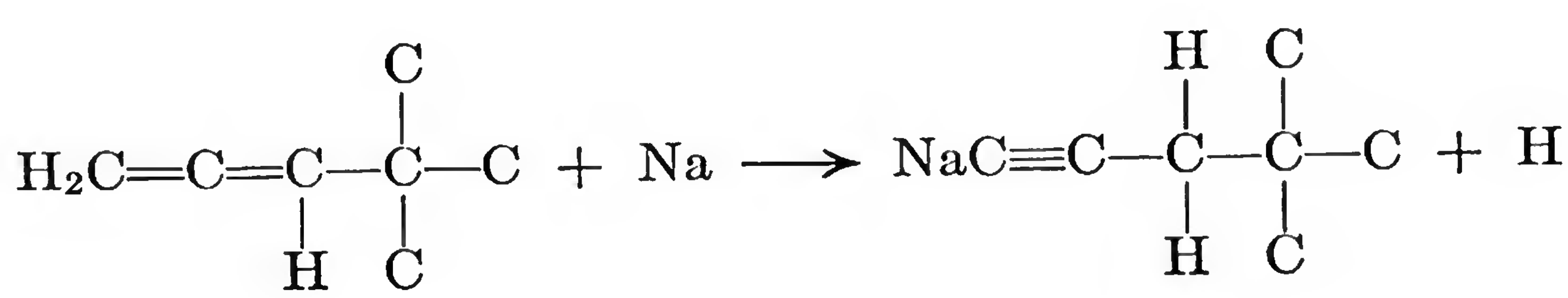
Heptadiene-1,2 (*n*-butylallene) with xylene or petroleum of boiling point above 180°, treated for 2 hours at 140° with a slight excess of sodamide (suspended in Vaseline), gave the sodium derivative of heptyne-1 and liberated free ammonia.[79]

$$\mathrm{C{=}C{=}C{-}C{-}C{-}C{-}C \longrightarrow C{\equiv}C{-}C{-}C{-}C{-}C{-}C}$$

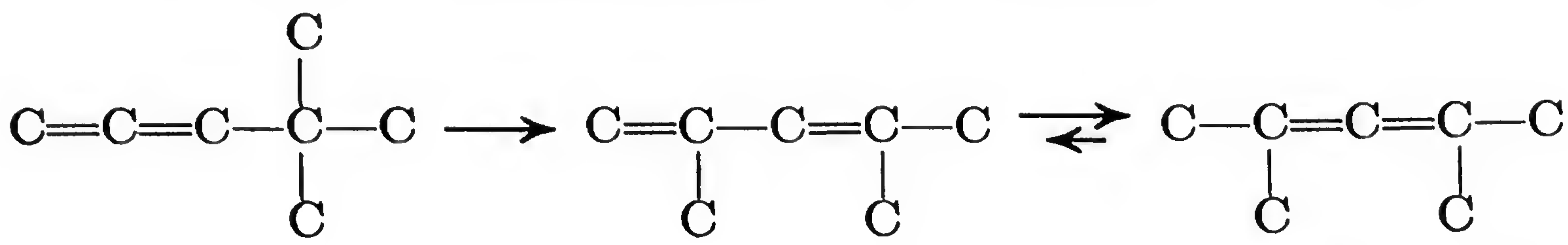
5-Methylhexadiene-1,2 (isobutylallene) gave the sodium derivative of 5-methylhexyne-1 in good yield [79] when treated with sodamide as in the foregoing experiment. Free ammonia was liberated at 100-120°.



4,4-Dimethylpentadiene-1,2 (*tert*-butylallene), heated with sodium, formed the sodium derivative of 4,4-dimethylpentyne-1.[182] This reaction involves the removal of 2 terminal hydrogens, one of these by a 3-carbon type of hydrogen migration and the other by displacement with sodium:

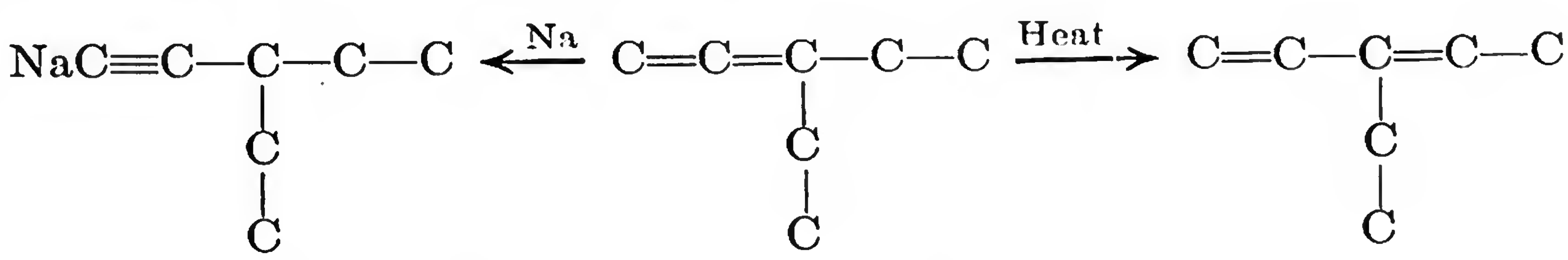


4,4-Dimethylpentadiene-1,2 (*tert*-butylallene), when passed over "Floridin" at 230-235°, gave successively 2,4-dimethylpentadiene-1,3 and 2,4-dimethylpentadiene-2,3 (tetramethylallene).[553] The equilibrium relationships, disregarding polymerization, favor complete transformation of 2,4-dimethylpentadiene-1,3 into 2,4-dimethylpentadiene-2,3, as demonstrated by a study of mixtures at 120-206° in the presence of "Floridin."[551] The initial formation of 2,4-dimethylpentadiene-1,3 merits further study; it may be considered as a rare instance of the shift of an alkyl and an unsaturated bond, *without* hydrogen transfer. This isomerization is patterned after the ordinary allylic rearrangement, and is part of the following "right-shift" of equilibrium:



2,4-Dimethylpentadiene-2,3, heated for 5 days at 150°, was largely polymerized, but part of it isomerized into 2,4-dimethylpentadiene-1,3 ("1,1-dimethylisoprene").[371] Heating with sodium or potassium at 125° gave similar results.[371] Since sodium converts 4,4-dimethylpentadiene-1,2 into the sodium derivative of 4,4-dimethylpentyne-1, the formation of this alkali-metal derivative from 2,4-dimethylpentadiene-2,3 is to be considered. An improbable "left-shift" of equilibrium beyond the unobserved reversion into 4,4-dimethylpentadiene-1,2 would be required.

3-Ethylpentadiene-1,2 (unsym-diethylallene), when heated, gave 3-ethylpentadiene-1,3 and polymers.[371] With sodium, it formed the sodium derivative of 3-ethylpentyne-1: [371]



The experimental data on the isomerization of allenic alkadienes are given in Table 11, p. 268.

Conclusions

1. Allenic alkadienes isomerize by formation of an alkyne or a conjugated alkadiene.
2. Catalysts for the formation of an alkyne are alcoholic potash, "Floridin," quinoline hydrobromide, sodamide, and sodium metal.
3. Alumina, "Floridin," quinoline hydrobromide, and heat alone are used in isomerizations yielding conjugated alkadienes.

Non-Allenic Alkadienes

Some work has been carried out on the isomerization of non-allenic alkadienes. Isomerization [204] of 2-methylbutadiene-1,3 into 3-methylbutadiene-1,2, by heating with weak alcoholic hydrochloric acid, could not be duplicated by another experimenter.[325] The available data indicate that the process gives 3-chloro-3-methylbutene-1, instead of an isomeric hydrocarbon.

Hexadiene-1,4 (*i.e.*, allylpropenyl) gave hexadiene-2,4 (*i.e.*, dipropenyl) when heated at 100° for 6 hours with concentrated alcoholic potash.[231]

Hexadiene-1,5 (*i.e.*, diallyl) upon passage through a "Pyrex" vessel at 500°, with carbon dioxide as diluent, probably gave some hexadiene-1,4 and hexadiene-2,4.[261, 262] Hexadiene-1,5 was 10 per cent isomerized

when heated at 250° for 10 days.[331] Six passes of hexadiene-1,5 over "Floridin" at 225° yielded 41.5 per cent of hexadiene-2,4.[333] A 73.4 per cent yield of hexadiene-2,4 was obtained by passage of hexadiene-1,5 with carbon dioxide over palladium-asbestos at 200°, then over platinized carbon at 200°, and again at 300°.[337] Alumina, as catalyst, converted hexadiene-1,5 into 69 per cent of hexadiene-2,4 at 300° and into 83 per cent at 360°.[338] Hexadiene-1,5 yielded 3 per cent of hexadiene-1,3 and 39 per cent of hexadiene-2,4 when subjected to alumina at 365°.[593a] Chromia effected an isomerization to hexadiene-2,4, which increased from 14.3 per cent at 225° under high feed velocity to 60.9 per cent at 275° and moderate feed velocity.[343]

Hexadiene-1,5, heated 6 hours at 170° with alcoholic potash, gave hexadiene-2,4 and probably some hexyne-3.[179] The reaction is incomplete, since the product formed contained unchanged diallyl. The following equations are proposed as an explanation of the formation of hexyne-3 (the catalyst is probably C_2H_5OK):

$$H_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + 2C_2H_5OH \longrightarrow \left[H_3C{-}\underset{\underset{OC_2H_5}{|}}{CH}{-}CH_2{-}CH_2{-}\underset{\underset{OC_2H_5}{|}}{CH}{-}CH_3\right]$$

$$\left[H_3C{-}\underset{\underset{OC_2H_5}{|}}{CH}{-}CH_2{-}CH_2{-}\underset{\underset{OC_2H_5}{|}}{CH}{-}CH_3\right] \longrightarrow H_3C{-}CH{=}CH{-}CH{=}CH{-}CH_3 + 2C_2H_5OH$$

$$H_3C{-}CH{=}CH{-}CH{=}CH{-}CH_3 + 2C_2H_5OH \longrightarrow \left[H_3C{-}CH_2{-}\underset{\underset{C_2H_5O}{|}}{CH}{-}\underset{\underset{OC_2H_5}{|}}{CH}{-}CH_2{-}CH_3\right]$$

$$\left[H_3C{-}CH_2{-}\underset{\underset{C_2H_5O}{|}}{CH}{-}\underset{\underset{OC_2H_5}{|}}{CH}{-}CH_2{-}CH_3\right] \longrightarrow H_3C{-}CH_2{-}C{\equiv}C{-}CH_2{-}CH_3 + 2C_2H_5OH$$

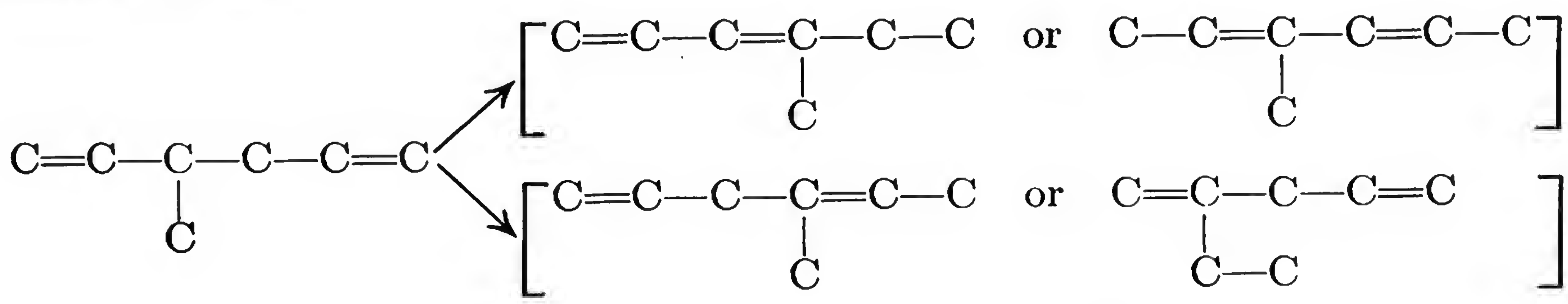
Hexadiene-2,4, when passed over alumina at 360°, gave about 15 per cent of hexadiene-1,3 and 2 per cent of hexadiene-1,4; elevation of temperature to 450-480° resulted in a ten-fold increase in the amount of hexadiene-1,4, together with the formation of pentadiene-1,3 as a new product.[445]

Heptadiene-1,5 was transformed into 6 per cent of heptadiene-2,4 and 8 per cent of 3-methylhexadiene-1,5 by a single passage over alumina at 365°.[593a] These isomerizations proceed respectively by migrations of 2 hydrogen atoms (from 3-position into 1-position and from 4-position into 2- or 6-position, referred to the initial chain) and by transfer of a hydrogen atom for a methyl group:

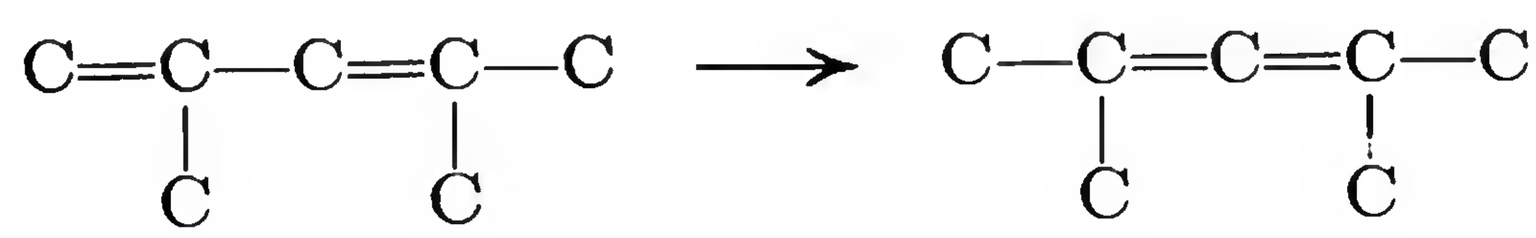
$$H_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_3 \begin{array}{l} \nearrow H_3C{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}CH_3 \\ \\ \searrow H_2C{=}CH{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}CH{=}CH_2 \end{array}$$

2-Methylhexadiene-1,5 yielded 58 per cent of 2-methylhexadiene-2,4 when passed once over alumina at 365°.[593a] In this example, both double bonds shift toward a conjugated position, and the final molecule acquires a more stable, terminal isopropylidene, structure (analogous to "trimethylethylene"):

3-Methylhexadiene-1,5 was isomerized both to conjugated and non-conjugated isomers upon passage over alumina at 365°.[593a] The conjugated isomer (14 per cent) was either 4-methylhexadiene-1,3 or 3-methylhexadiene-2,4, whereas the non-conjugated product (18 per cent) was either 4-methylhexadiene-1,4 or 2-ethylpentadiene-1,4. These products involved the shift of one or both double bonds; the initial carbon chain remained intact:

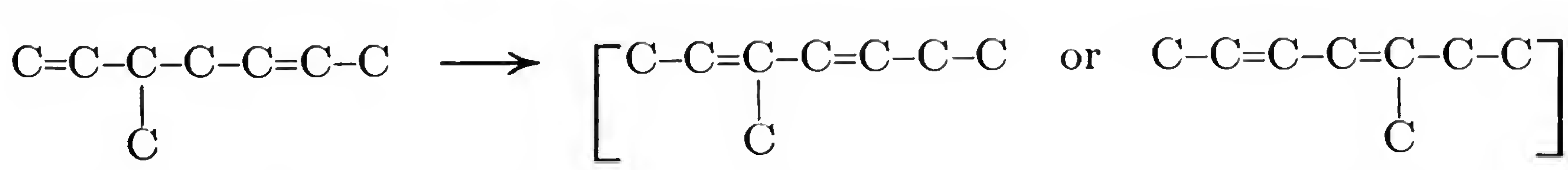


2,4-Dimethylpentadiene-1,3, when passed over "Floridin" at 204° [551] or 230-235°,[553] isomerized into 2,4-dimethylpentadiene-2,3 (*i.e.*, tetramethylallene). In this reaction, a double bond shifts toward the center of the molecule:



Octadiene-2,6 probably yielded a small quantity of octadiene-3,5 when conducted over alumina at 365°.[593a] The product contained 72 per cent of unconverted octadiene-2,6.

3-Methylheptadiene-1,5 gave 4 per cent of an isomer, which was either 3- or 5-methylheptadiene-2,4, upon a single passage over alumina at 365°.[593a] These products would involve the shift of both or only one double bond, respectively:



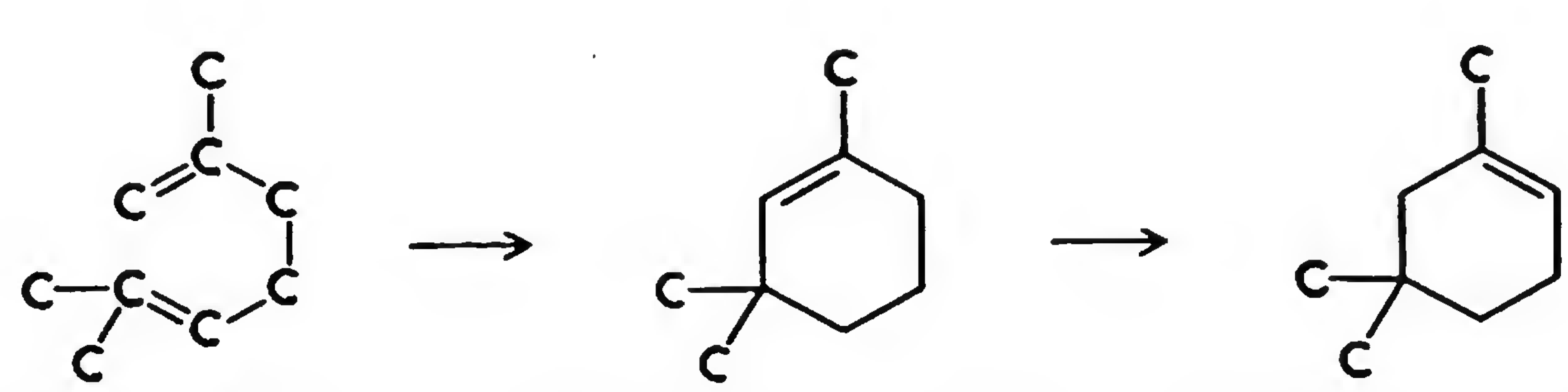
2,5-Dimethylhexadiene-1,5 (*i.e.*, diisobutenyl), when heated at 180° for 4 hours with alcoholic potash, gave unchanged diisobutenyl and 2,5-dimethylhexadiene-2,4 (*i.e.*, diisocrotyl),[179] the last substance representing a shift of 2 double bonds toward the center of the molecule. The reaction was interpreted as follows:

$$H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + 2C_2H_5OH \longrightarrow \left[H_3C{-}\overset{\displaystyle OC_2H_5}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_2{-}\overset{\displaystyle OC_2H_5}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3\right]$$

$$\left[H_3C{-}\overset{\displaystyle OC_2H_5}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_2{-}\overset{\displaystyle OC_2H_5}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3\right] \longrightarrow H_3C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 + 2C_2H_5OH$$

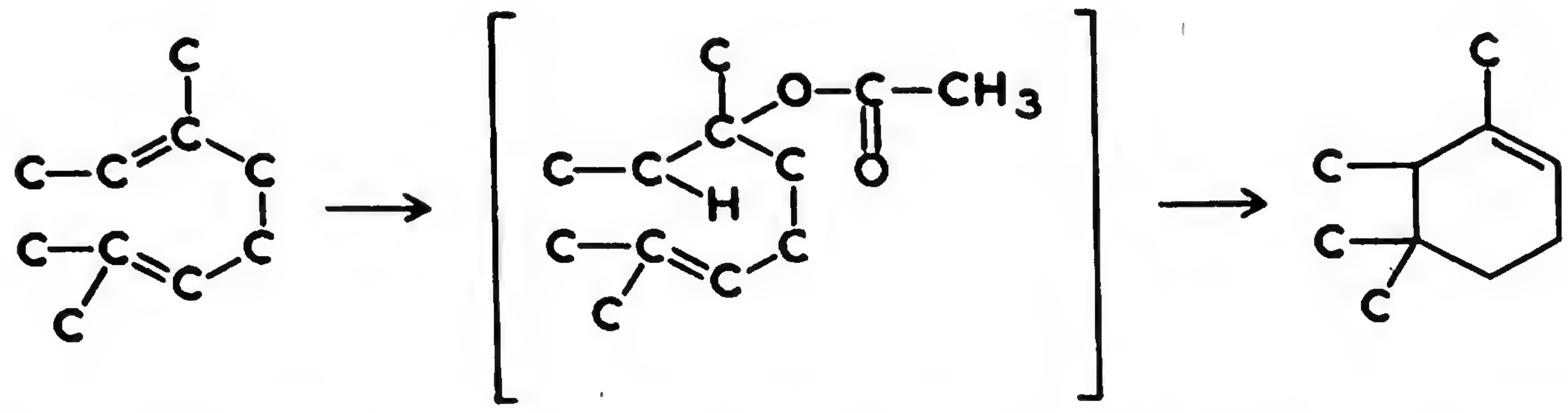
2,5-Dimethylhexadiene-1,5, when passed once over "Floridin" at 205-210°, gave 70 per cent of 2,5-dimethylhexadiene-2,4.[333] Alumina is a catalyst at 220-225° for the same reaction.[338] An 81 per cent yield of 2,5-dimethylhexadiene-2,4 is readily obtainable from 2,5-dimethylhexadiene-1,5 upon passage over alumina at 365°.[593a] Other, less efficient catalysts may be employed, *e.g.*, ferric chloride, magnesium chloride, or potassium hydroxide. The isomerization proceeds slowly at the ebullition point, 114.4°, in an uncatalyzed system.[593a]

From the foregoing experiments, it is evident that non-conjugated alkadienes exhibit a tendency to conjugate. Cyclization, which is a type of isomerization due to an intramolecular alkylation, may occur in the presence of acidic catalysts. 2,6-Dimethylheptadiene-1,5 (geraniolene), upon contact with 65-per cent sulfuric acid for 3 days,[582] or when heated at 100° for 4 hours with 60-per cent sulfuric acid,[583] undergoes a cyclization into the isomers, α- and β-cyclogeraniolenes. These isomerizations are largely controlled by temperature, since considerable loss by resinification occurs with sulfuric acid (sp. gr. 1.56) at temperatures above 15°.[632] α-Cyclogeraniolene is the principal component of the isomeric mixture:[632]



Geraniolene β-Cyclogeraniolene α-Cyclogeraniolene

2,6-Dimethyloctadiene-2,6 [167, 168] probably represents the structure of both Semmler's linaloolene [531] and dihydromyrcene.[532] These substances undergo cyclization when treated with acids. Linaloolene heated 20 minutes at 100° with concentrated sulfuric acid gave cyclolinaloolene,[531] whereas dihydromyrcene, when treated with acetic acid plus sulfuric acid, gave cyclodihydromyrcene.[147, 515, 532] From the proposed structures of cyclodihydromyrcene [147, 532] and that of the intermediate dihydrolinalyl acetate,[515] the last reaction can be expressed as follows:



Dihydromyrcene (Linaloolene) — Dihydrolinalyl acetate — Cyclodihydromyrcene (Cyclolinaloolene) ("α-Cyclomethylgeraniolene")

This reaction should be reinvestigated in order to determine: (a) the extent to which acetic acid acts as a solvent; (b) the extent to which sulfuric acid enters into sulfate formation, and (c) the mechanism of ring closure in alkadienes of this type.

Experimental data on the isomerization of non-allenic alkadienes are given in Table 12, p. 274.

Conclusions

1. Non-allenic alkadienes generally isomerize by a shifting of the double bonds into closer positions (allenic and conjugated).
2. Alumina, "Floridin," and alcoholic potash are typical catalysts for shifting the double bonds of non-allenic alkadienes.
3. Cyclization is the result of treatment with sulfuric acid.

Alkapolyenes

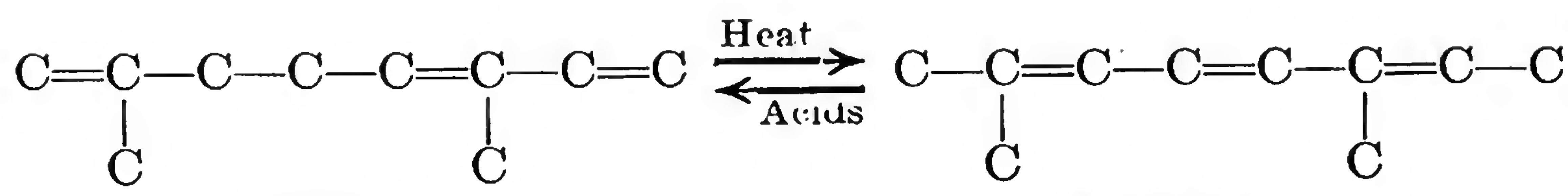
Isomerizations

6-Methylheptatriene-1,2,3, when heated at 110-120° with potassium, gave the potassium derivative of 6-methylhepten-3-yne-1, together with hydrogen:[227]

$$\mathrm{C{=}C{=}C{=}C{-}C{-}\underset{\displaystyle C}{\underset{|}{C}}{-}C} + \mathrm{K} \longrightarrow \mathrm{K{-}C{\equiv}C{-}C{=}C{-}C{-}\underset{\displaystyle C}{\underset{|}{C}}{-}C} + 1/2\mathrm{H_2}$$

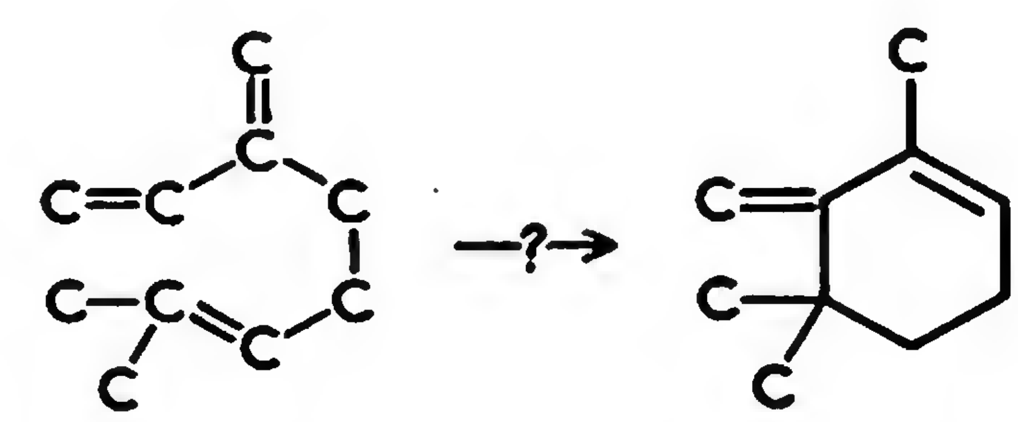
2,6-Dimethyloctatriene-1,5,7 (the acyclic terpene, ocimene), while heated under reflux for nearly 4 hours, formed 82 per cent of a conjugated isomer, 2,6-dimethyloctatriene-2,4,6 (allo-ocimene).[167]

2,6-Dimethyloctatriene-2,4,6 (the acyclic terpene, allo-ocimene), when treated with glacial acetic acid containing sulfuric acid, was re-formed very rapidly, though incompletely, into 2,6-dimethyloctatriene-1,5,7 (ocimene).[167, 169] This reaction was accompanied by polymerization. Allo-ocimene, upon being heated alone for one hour at 250-300° and then for 0.5 hour at 320°, was converted into an isomeric terpene (23.8 per cent) and polymers (38 per cent).[8]



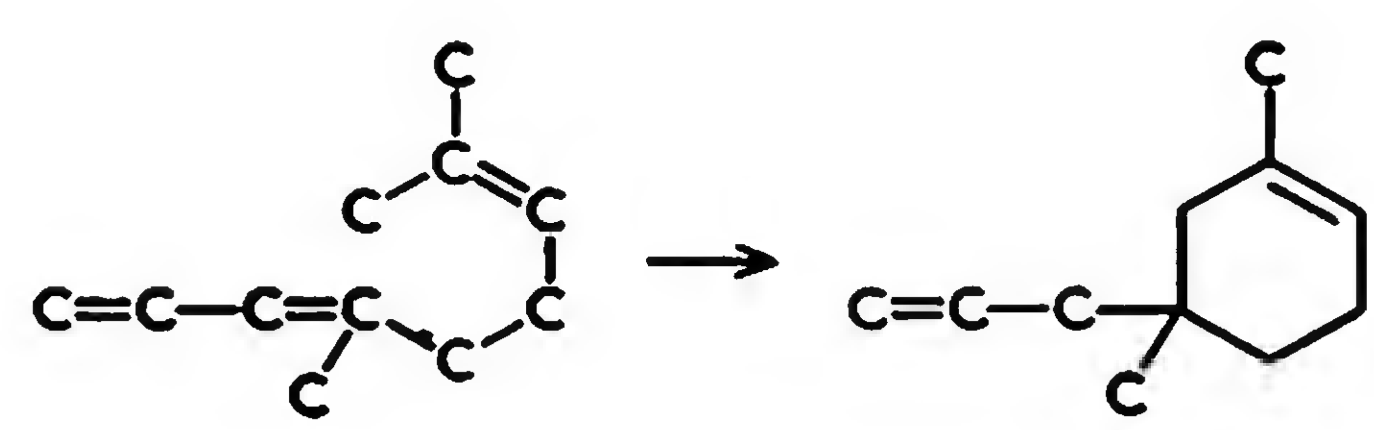
Ocimene Allo-Ocimene

3-Methylene-7-methyloctadiene-1,6 (the acyclic terpene, myrcene), when heated at 300° for 4 hours, gave polymyrcenes and probably cyclomyrcene:[243]

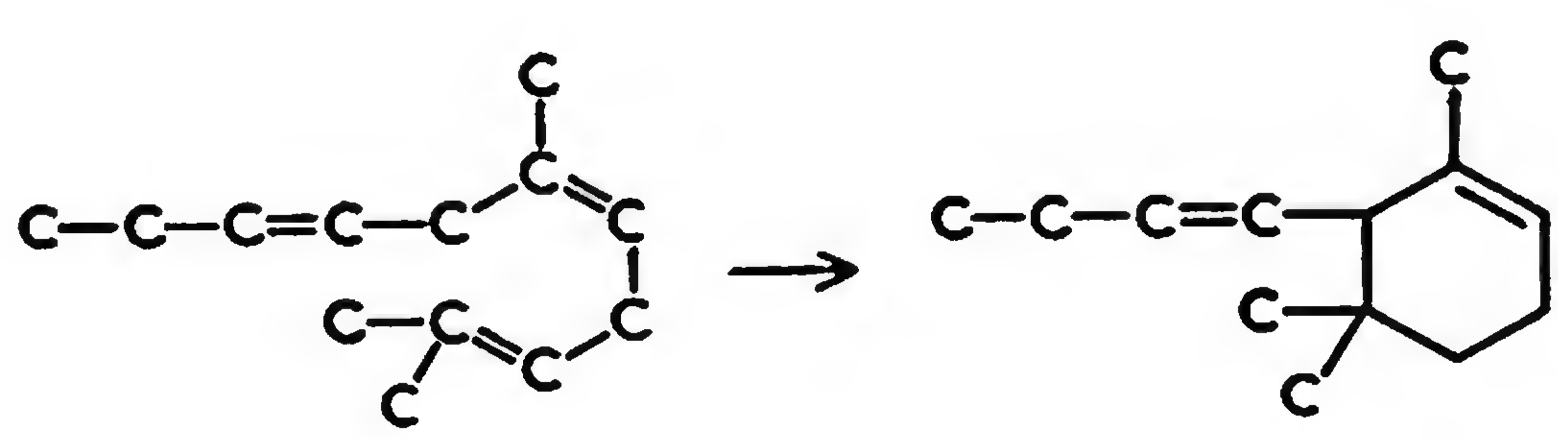


MYRCENE CYCLOMYRCENE

4,8-Dimethylnonatriene-1,3,7, when treated with 80-per cent sulfuric acid, was cyclized into 1,5-dimethyl-5-allylcyclohexene-1:[226]



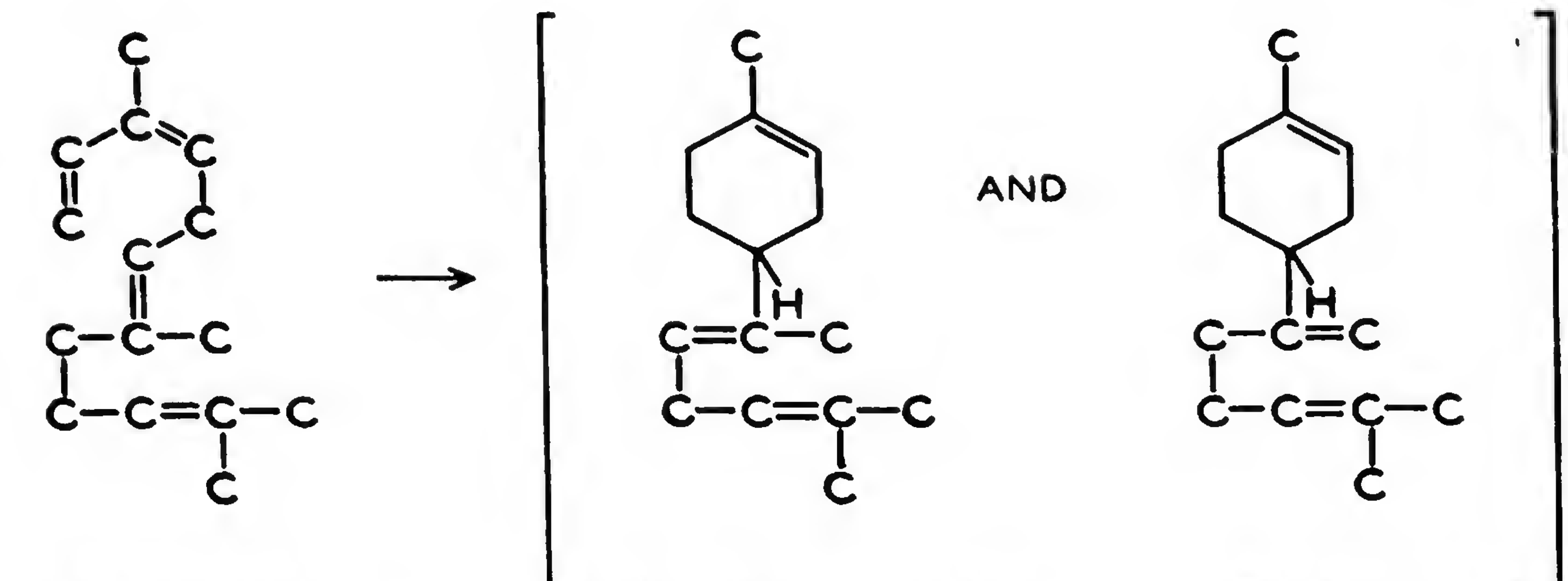
2,6-Dimethylundecatriene-2,5,8 ("pseudoionane") upon being heated with acetic acid containing 2.5 per cent of sulfuric acid, formed 1,5,5-trimethyl-6-(1-butenyl)cyclohexene-1 ("α-ionane"):[304]



"PSEUDOIONANE" "α-IONANE"

Treatment of the slightly optically active aliphatic sesquiterpene "sesquicitronellene" (from Java citronella oil) with formic acid gave a strongly dextrorotatory cyclic product: "cyclosesquicitronellene."[539] This reaction is stated to be an isomerization of farnesene into bisabolene,[486] and may be interpreted as the conversion of 3,7,11-trimethyldodecatetraene-1,3,6,10 (α-farnesene) into *d*-α- and *d*-β-bisabolenes (the "*d*-limonene of the sesquiterpenes"):*

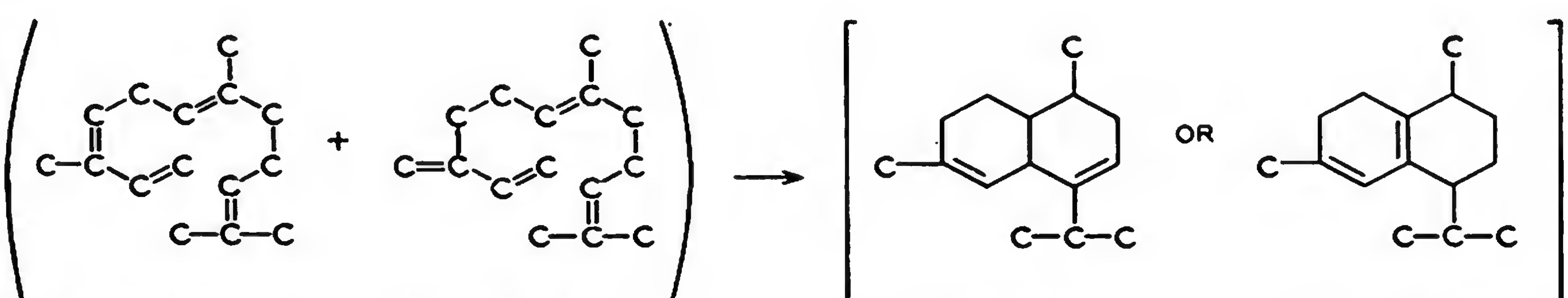
* Throughout the text and tables of this book, care has been exercised in using configurational notations; the lower-case letters *d*- and *l*- denote discriminately the actual optical rotations of isomers.



α-FARNESENE d-α-BISABOLENE d-β-BISABOLENE

The actual course of this isomerization is unusual in that the formation of *d*-rotatory bisabolenes predominates.

A mixture of α- and β-farnesenes, when treated with acetic acid containing sulfuric acid, formed a hexahydrocadalene and α-bisabolyl acetate:[486]

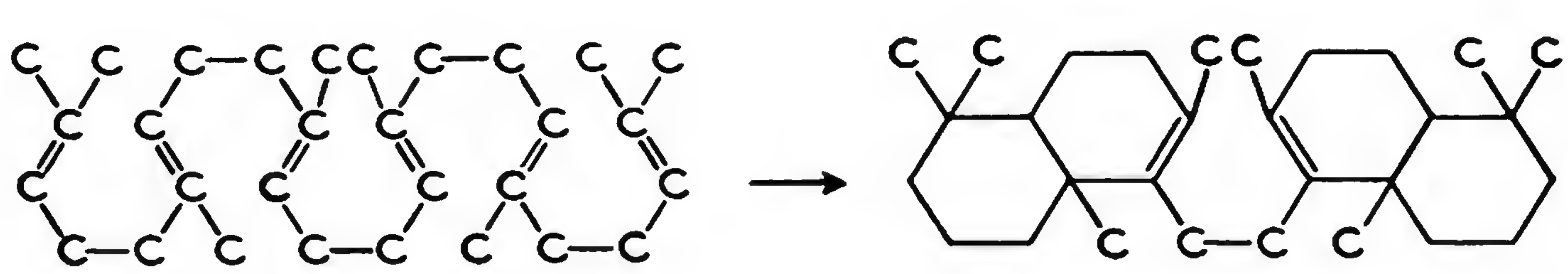


α-FARNESENE β-FARNESENE α-CADINENE ISOCADINENE

"HEXAHYDROCADALENE"

Treatment of a similar α- and β-farnesene mixture with 90-per cent formic acid at 120° gave a monocyclic sesquiterpene product of low optical activity, probably a mixture of α- and β-bisabolenes.[482]

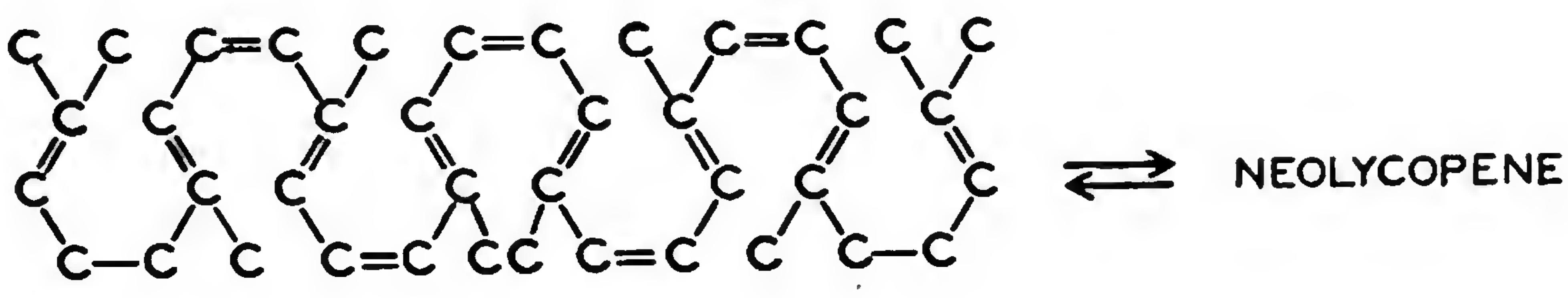
2,6,10,15,19,23 - Hexamethyltetracosahexaene - 2,6,10,14,18,22 (*i. e.*, squalene) underwent multi-cyclization when boiled with 98-per cent formic acid. Isomerizations of squalene for periods of one-half hour, 3 hours, and 3 days yielded "dicyclosqualene," "tricyclosqualene," and "tetracyclosqualene," respectively.[244] The action of a mixture of sulfuric acid and acetic anhydride upon squalene, for 2.5 hours under reflux, probably resulted in the formation of "dicyclosqualene;" a corresponding 18-hour reflux with alcoholic sulfuric acid probably gave "tricyclosqualene."[244]



SQUALENE "TETRACYCLOSQUALENE"

2,6,10,14,19,23,27,31-Octamethyldotriacontatridecaene - 2,6,8,10,12,14,-16,18,20,22,24,26,30 (*i.e.*, lycopene, $C_{40}H_{56}$) isomerized spontaneously to neolycopene within a few days in the presence of benzene or petroleum

ether as solvents.[660] The conversion proceeded more rapidly at elevated temperatures. The structure of neolycopene is unknown, but that of lycopene [295] is suited preeminently for cyclization:



LYCOPENE

Iodine in benzene is an effective catalyst at room temperature both for the isomerization of lycopene into neolycopene, and for the reverse reaction.[661] The ease of reversibility of the reaction may indicate a *cis-trans* isomerization rather than a cyclization-decyclization.

The experimental data on isomerization of alkapolyenes are given in Table 13, p. 280.

Conclusions

Alkapolyenes isomerize by transfer of double bonds, conversion of 2 double bonds into a triple bond, and by cyclization or multi-cyclization.

Chapter III

Alkynes, Alkadiynes, and Alkapolyynes

Alkynes

Isomerizations

The isomerization plus thermolysis of alkynes-1 at 500-600° has been summarized as follows: "At moderate temperatures, polymerization sets in at a rate which must increase with the temperature. At significantly higher threshold temperatures, however, two other effects are noted: (1) partial decomposition into simpler products, and (2) partial isomerization into 1,2-alkadienes. It is noteworthy that the temperature required for the isomerization is about the same as that required for the decomposition into gases." [263]

Alkynes, under the influence of alcoholic alkali, undergo isomerization by shifting the position of their triple bond or by forming an allene. Alcoholic potassium hydroxide and alcoholic sodium hydroxide are used interchangeably.[180] Isomerization is possible even among the alkapolyynes, but without the use of alkali.[132, 499, 563] Thermal and 3-carbon-system isomerizations of alkynes have been discussed in Chapter II under Alkadienes. The number of isomeric alkynes is given in Tables 14 and 15.

Propyne (*i.e.*, methylacetylene or allylene), heated at 170-180° with alcoholic potash for 12 hours, incompletely forms ethyl isopropenyl ether.[178] This ether is stable at 170-180°, whereas ethers from larger alkynes are unstable even at 130-140°. Propadiene (allene) was not reported as a product, which is an unexpected observation, since the same ether is formed *incompletely* from propadiene under similar conditions. The conversion of the ether into allene may be either a very slow reaction or one difficult to effect:

$$HC{\equiv}C{-}CH_3 + C_2H_5OH \rightleftarrows \underset{\displaystyle OC_2H_5}{H_2C{=}\overset{}{C}}{-}CH_3 \longleftarrow H_2C{=}C{=}CH_2 + C_2H_5OH$$

Propyne, upon thermolysis or when treated with alpha particles, is believed to undergo an initial conversion into propadiene.[156] The pyrolysis of propyne at 555° yielded about 14 per cent of hydrocarbons soluble in 82.4-per cent sulfuric acid, besides 28 per cent of liquids taken to be polymers of propadiene.[370a] The dissolved hydrocarbons were probably

Table 14. Number of Isomeric Hydrocarbons of the Alkyne Series (Excluding the additional isomers due to stereoisomerism and alkadienes)

From Coffman, Blair, and Henze [110]

Carbon content	Number of Isomers
2	1
3	1
4	2
5	3
6	7
7	14
8	32
9	72
10	171
11	405
12	989
13	2,426
14	6,045
15	15,167
16	38,422
17	97,925
18	251,275
19	648,061
20	1,679,869
21	4,372,872
22	11,428,365
23	29,972,078
24	78,859,809
25	208,094,977
26	550,603,722
27	1,460,457,242
28	3,882,682,803
29	10,344,102,122
30	27,612,603,765

propadiene with a little propene. Propyne passed over "Floridin" at 180-363°, gave propadiene and polymers.[552]

Butyne-1 (*i.e.*, ethylacetylene) partially isomerized into butyne-2 (dimethylacetylene) when heated at 170° for 16 hours in the presence of alcoholic potash.[176, 180] The following equations for the reaction were given;[176] they seem to be correct, with the possible exception of the reaction yielding *free* butadiene-1,2 and effected by free ethanol:

$$HC{\equiv}C{-}CH_2{-}CH_3 + C_2H_5OK \longrightarrow \left[\begin{array}{l} KHC{=}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}{-}CH_2{-}CH_3 \end{array}\right]$$

$$\left[\begin{array}{l} KHC{=}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}{-}CH_2{-}CH_3 \end{array}\right] + C_2H_5OH \longrightarrow H_2C{=}C{=}CH{-}CH_3 + C_2H_5OK + C_2H_5OH$$

$$H_2C{=}C{=}CH{-}CH_3 + C_2H_5OK \longrightarrow \left[\begin{array}{l} KH_2C{-}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}{=}CH{-}CH_3 \end{array}\right]$$

$$\left[\begin{array}{l} KH_2C{-}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}{=}CH{-}CH_3 \end{array}\right] + C_2H_5OH \longrightarrow H_3C{-}C{\equiv}C{-}CH_3 + C_2H_5OK + C_2H_5OH$$

Table 15. Isomeric Alkynes.

From Coffman [109]

	RC≡CH		RC≡CR′		RC≡CH and RC≡CR′		
Carbon content	Stereo	Non-stereo	Stereo	Non-stereo	Total stereo	Total Non-stereo	Total isomers
3	0	1	0	0	0	1	1
4	0	1	0	1	0	2	2
5	0	2	0	1	0	3	3
6	2	3	0	3	2	6	8
7	6	5	2	5	8	10	18
8	20	8	8	11	28	19	47
9	60	14	30	19	90	33	123
10	176	23	101	38	277	61	338
11	512	39	316	68	828	107	935
12	1,488	65	975	129	2,463	194	2,657
13	4,326	110	2,948	232	7,274	342	7,616
14	12,648	184	8,878	428	21,526	612	22,138
15	37,186	310	26,622	768	63,808	1,078	64,886
16	109,980	520	79,980	1,393	189,960	1,913	191,873
17	327,216	876	240,590	2,487	567,806	3,363	571,169
18	979,020	1,471	726,238	4,460	1,705,258	5,931	1,711,189
19	2,944,414	2,475	2,199,070	7,924	5,143,484	10,399	5,153,883
20	8,897,732	4,159	6,683,108	14,095	15,580,840	18,254	15,599,094
21	27,004,290	6,996	20,378,720	24,925	47,383,010	31,921	47,414,931
22	82,287,516	11,759	62,347,546	44,065	144,635,062	55,824	144,690,886

The isomerization of butyne-1 by alcoholic alkali is always incomplete.[176, 180, 653] There are no indications that isomerizations with such alkali may be reversible. Butyne-1 formed butadiene-1,2 when passed over "Floridin" at 275°.[554] However, butadiene-1,3 resulted when pumice was utilized as the catalyst at 300°.[141a]

Butyne-2 was isomerized into butadiene-1,2 and butyne-1 upon passage over "Floridin" at 278-285°.[554] This reaction is opposite in direction to that observed when alcoholic alkali acts upon butyne-1. Possibly the "Floridin" acts as an "acidic" catalyst temporarily supplying a proton:

$$\mathrm{C{-}C{\equiv}C{-}C + HX \longrightarrow C{-}\underset{\textstyle X}{\underset{|}{C}}{=}C{-}C \longrightarrow C{=}C{=}C{-}C + HX \rightleftarrows C{=}\underset{\textstyle X}{\underset{|}{C}}{-}C{-}C \rightleftarrows C{\equiv}C{-}C{-}C + HX}$$

Pentyne-1 (propylacetylene), heated 24 hours at 170° with alcoholic potash, gave pentyne-2 (methylethylacetylene).[176, 180] Isomerization occurred even at 30° or 40°.[180]

$$\mathrm{C{\equiv}C{-}C{-}C{-}C \longrightarrow C{-}C{\equiv}C{-}C{-}C}$$

Pentyne-2, when heated for 4-5 hours at 100° with less than one mole portion of sodium, gave the sodium derivative of pentyne-1, hydrolyzed by water to the last alkyne.[177] This reaction, which is opposite in character to that with alcoholic potash, was expressed as follows:

$$\mathrm{3H_3C{-}C{\equiv}C{-}C_2H_5 + 2Na \longrightarrow 2NaC{\equiv}C{-}C_3H_7 + H_3C{-}CH{=}CH{-}C_2H_5}$$

The presence of pentene-2 was not established definitely; its formation accounts for the hydrogen loss in forming the sodium derivative.

3-Methylbutyne-1 (isopropylacetylene), heated for 6 hours at 150° with alcoholic potash, gave 3-methylbutadiene-1,2 (unsym-dimethylallene).[176, 180] Increasing the temperature to 170° resulted in polymerization of the allenic alkadiene. The isomerization was explained by two equations:[176]

$$\mathrm{HC{\equiv}C{-}\underset{\textstyle CH_3}{\underset{|}{CH}}{-}CH_3 + C_2H_5OK \longrightarrow \left[KHC{=}\underset{\textstyle C_2H_5O}{\underset{|}{C}}{-}\underset{\textstyle CH_3}{\underset{|}{CH}}{-}CH_3\right]}$$

$$\mathrm{\left[KHC{=}\underset{\textstyle C_2H_5O}{\underset{|}{C}}{-}\underset{\textstyle CH_3}{\underset{|}{CH}}{-}CH_3\right] + C_2H_5OH \longrightarrow H_2C{=}C{=}\underset{\textstyle CH_3}{\underset{|}{C}}{-}CH_3 + C_2H_5OK + C_2H_5OH}$$

Alumina catalyzed the isomerization of 3-methylbutyne-1 into 2-methylbutadiene-1,3 (isoprene) at 400°,[29, 32, 639] which corresponds to the fact that alumina at 300° converted 3-methylbutadiene-1,2 (unsym-dimethylallene) into isoprene.[31] 3-Methylbutyne-1 and "Floridin" at 270° gave a little 3-methylbutadiene-1,2 and a trace of isoprene.[548]

$$\mathrm{C{\equiv}C{-}\underset{\textstyle C}{\underset{|}{C}}{-}C \longrightarrow \left[C{=}C{=}\underset{\textstyle C}{\underset{|}{C}}{-}C\right] \longrightarrow C{=}\underset{\textstyle C}{\underset{|}{C}}{-}C{=}C}$$

Heating of hexyne-1 at 500°, 550°, and 600° gave some hexadiene-1,2, and at 600° also a trace of hexyne-2.[263] A partial conversion into decomposition products occurred in all the experiments.

$$C{\equiv}C{-}C{-}C{-}C{-}C \begin{array}{l} \nearrow C{=}C{=}C{-}C{-}C{-}C \\ \searrow C{-}C{\equiv}C{-}C{-}C{-}C \end{array}$$

Hexyne-2 (methylpropylacetylene) yielded the sodium derivative of hexyne-1 in the presence of sodium at 150-160°.[177] The reaction was given as:

$$3H_3C{-}C{\equiv}C{-}C_3H_7 + 2Na \longrightarrow 2NaC{\equiv}C{-}C_4H_9 + C_6H_{12}$$

3,3-Dimethylbutyne (*tert*-butylacetylene) did not isomerize even when heated for 16 hours at 200° with alcoholic potash,[176, 180] a fact that is in agreement with the theory of "the unstable ethyl ether."[176]

The isomerization plus thermolysis of heptyne-1 at 600° gave some heptadiene-1,2, a trace of heptyne-2, besides simpler decomposition products.[263] Isomerization of heptyne-1 upon passage over pumice at 350° has been observed also.[234]

$$C{\equiv}C{-}C{-}C{-}C{-}C{-}C \begin{array}{l} \nearrow C{=}C{=}C{-}C{-}C{-}C{-}C \\ \searrow C{-}C{\equiv}C{-}C{-}C{-}C{-}C \end{array}$$

Heptyne-1, heated with alcoholic potash at 140-150° for either 24 hours[42] or 36 hours,[41] was converted completely into heptyne-2. The isomerization of heptyne-1 (63 per cent preparation) was completed in 5 hours of treatment with potassium hydroxide and alcohol at 200°.[24] Dry soda-lime had no effect on heptyne-1 (76 per cent content, temperatures below 275°, periods up to 5 hours).[24] Passage of heptyne-1 (90 per cent pure) over soda-lime at 380° gave 70 per cent of heptyne-2.[234]

Treatment of heptyne-2 (80 per cent mixture containing some heptyne-1) with sodamide and mineral oil as diluent, at 160° for 12 hours, gave a final product containing 64 per cent of heptyne-1:[234]

$$C{-}C{\equiv}C{-}C{-}C{-}C{-}C \longrightarrow C{\equiv}C{-}C{-}C{-}C{-}C{-}C$$

Heptyne-3, when heated for 4 hours at 170° with sodamide and pseudocumene as diluent, formed 70-80 per cent of heptyne-1:[81]

$$C{-}C{-}C{\equiv}C{-}C{-}C{-}C \longrightarrow C{\equiv}C{-}C{-}C{-}C{-}C{-}C$$

Octyne-1 isomerized completely to octyne-2 when heated for 36 hours at 140-150° with alcoholic potash.[41, 42] The reverse reaction takes place with sodium. Octyne-2, heated for 8 hours on a sand bath with sodium, gave a 9 per cent yield of octyne-1 (after regeneration), together with

much unconverted octyne-2.[135] Similarly, octyne-2, heated for 36 hours in a sealed tube with sodium, first upon a water bath and then upon a salt bath, gave a 75 per cent yield of crude octyne-1.[43] Octyne-2, when heated for one hour at 150° with sodamide and pseudocumene as diluent, gave 80 per cent of octyne-1.[81]

$$\mathrm{C{\equiv}C{-}C{-}C{-}C{-}C{-}C{-}C} \underset{\mathrm{Na}}{\overset{\mathrm{C_2H_5OK}}{\rightleftarrows}} \mathrm{C{-}C{\equiv}C{-}C{-}C{-}C{-}C{-}C}$$

Octyne-3 isomerized into 55 per cent of octyne-1 when heated for 9 hours at 170° with sodamide and petroleum as a diluent:[81]

$$\mathrm{C{-}C{-}C{\equiv}C{-}C{-}C{-}C{-}C} \longrightarrow \mathrm{C{\equiv}C{-}C{-}C{-}C{-}C{-}C{-}C}$$

Nonyne-2, heated for 2 hours at 160° with sodamide and petroleum as diluent, gave 83 per cent of nonyne-1.[81]

$$\mathrm{C{-}C{\equiv}C{-}({-}C{-})_5{-}C} \longrightarrow \mathrm{C{\equiv}C{-}({-}C{-})_6{-}C}$$

In the study of isomerization of dodecyne-1 and dodecyne-2, and of hexadecyne-1 and hexadecyne-2, it was found that alcoholic potash changed the alkyne-1 to the alkyne-2, whereas sodium brought about the reverse reaction:[323]

$$\mathrm{C{\equiv}C{-}C{-}({-}C{-})_8{-}C} \underset{\mathrm{Na}}{\overset{\mathrm{C_2H_5OK}}{\rightleftarrows}} \mathrm{C{-}C{\equiv}C{-}({-}C{-})_8{-}C}$$

$$\mathrm{C{\equiv}C{-}C{-}({-}C{-})_{12}{-}C} \underset{\mathrm{Na}}{\overset{\mathrm{C_2H_5OK}}{\rightleftarrows}} \mathrm{C{-}C{\equiv}C{-}({-}C{-})_{12}{-}C}$$

Alkadiynes and Alkapolyynes

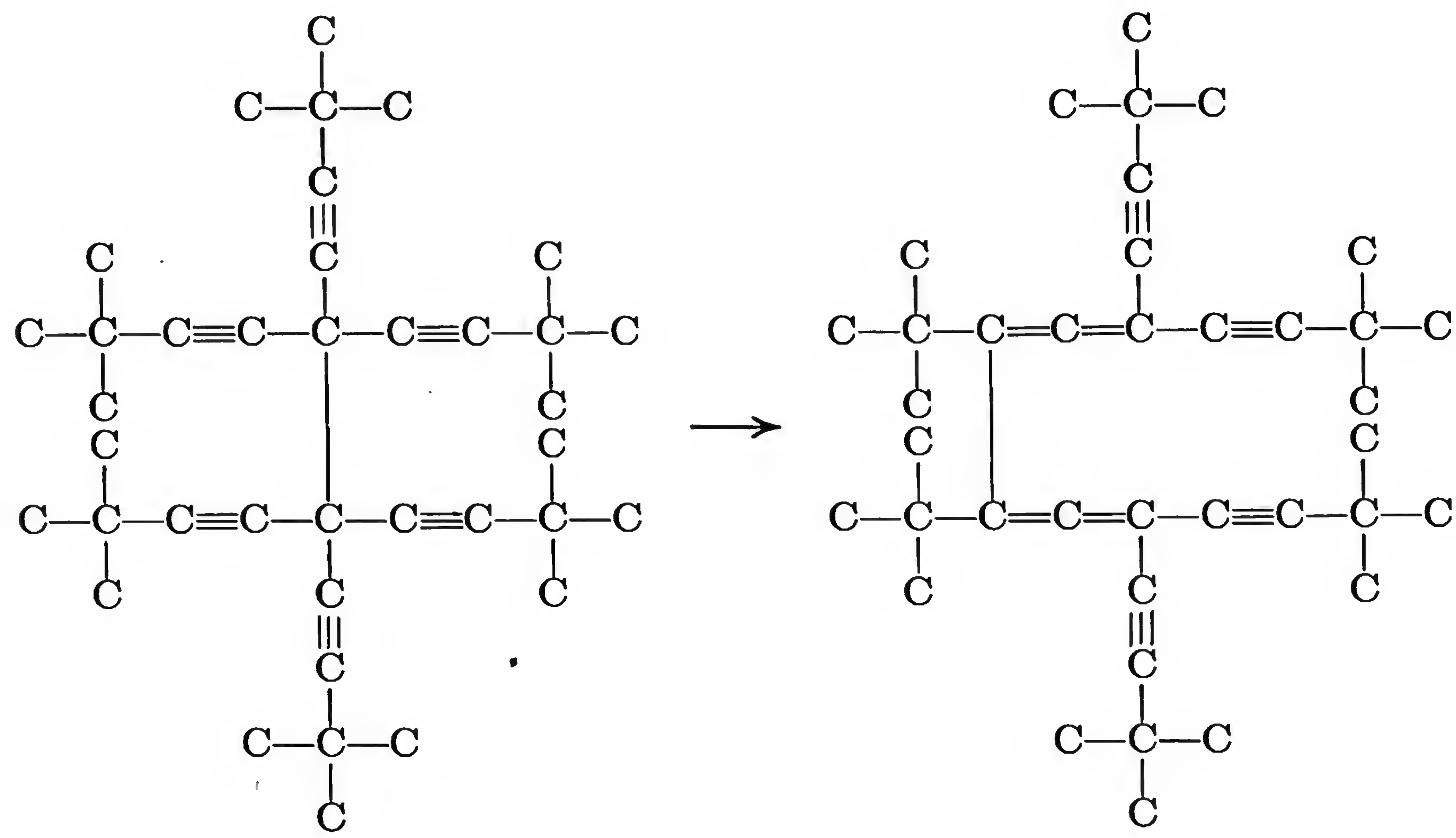
Isomerizations

Alkadiynes. In the isomerization of alkadiynes, hexadiyne-1,4 formed hexadiyne-2,4 when treated repeatedly with alcoholic potash under unspecified conditions.[336] Another observer,[231] however, has reported only polymerization by alcoholic potash. Hexadiyne-1,5 (*i.e.*, dipropargyl), heated at 100° for one hour with alcoholic potash, underwent a partial isomerization into hexadiyne-2,4.[179] An unsaturated ether, $C_8H_{12}O$, was isolated;[179] it is probably the intermediate responsible for one step of the isomerization. Pending further investigations, these reactions can be considered as the following right-shift of reactions:

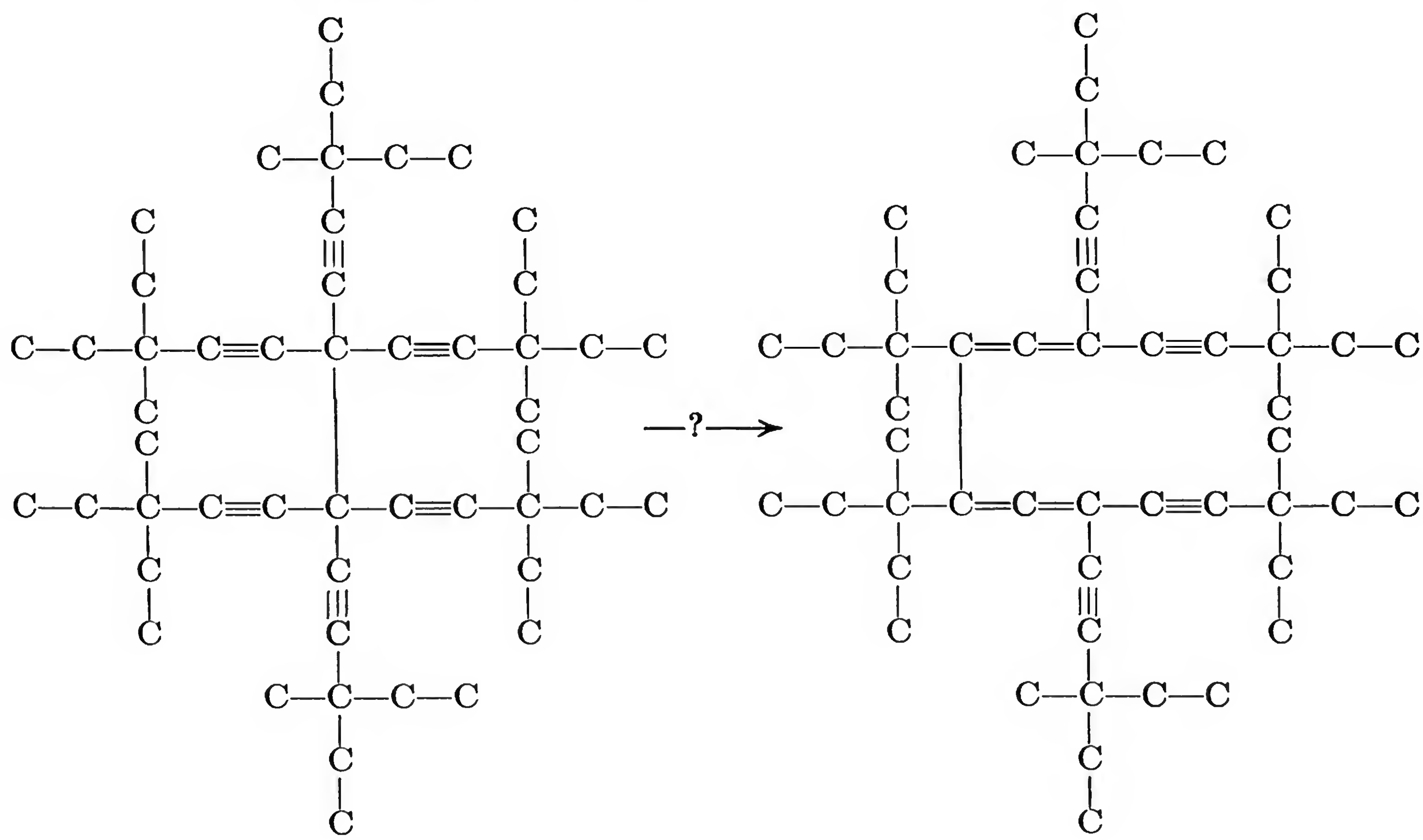
$$\mathrm{C{\equiv}C{-}C{-}C{-}C{\equiv}C} \longrightarrow \mathrm{C{\equiv}C{-}C{-}C{\equiv}C{-}C} \longrightarrow \mathrm{C{-}C{\equiv}C{-}C{\equiv}C{-}C}$$

Alkapolyynes. 2,2,9,9-Tetramethyl-5,5,6,6 - tetra-*tert* - butylethynyl-decadiyne-3,7 (*i.e.*, hexa-[*tert*-butylethynyl]-ethane), heated for one hour at 100° in alcoholic solution,[499] formed an isomer (40-60 per cent) to which has been assigned the diallenyl structure of 2,2,13,13-tetramethyl-5,10-di-*tert*-butylethynyl-7,8 - di - tert-butyl - tetradecatetraene - 5,6,8,9-diyne-3,11.[563] The same isomer was obtained by heating a xylene solu-

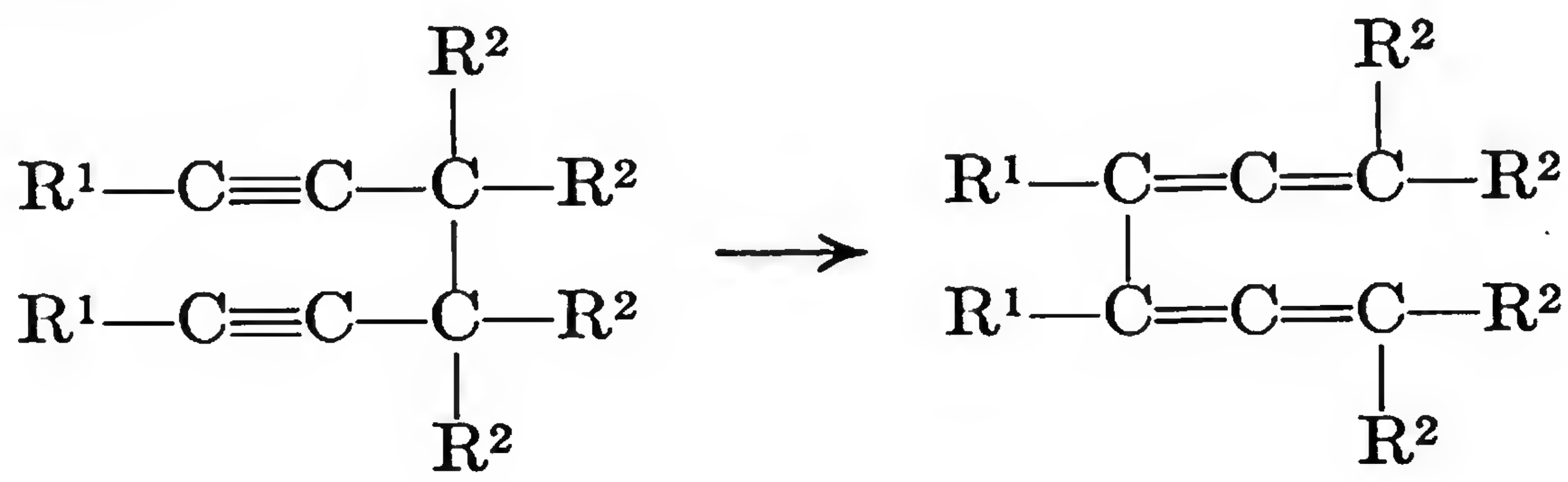
tion [499] and in an attempted reduction of the "ethane" by hydrogen under pressure at 70-80° in the presence of alcohol and a platinum black plus platinum oxide catalyst:[575]



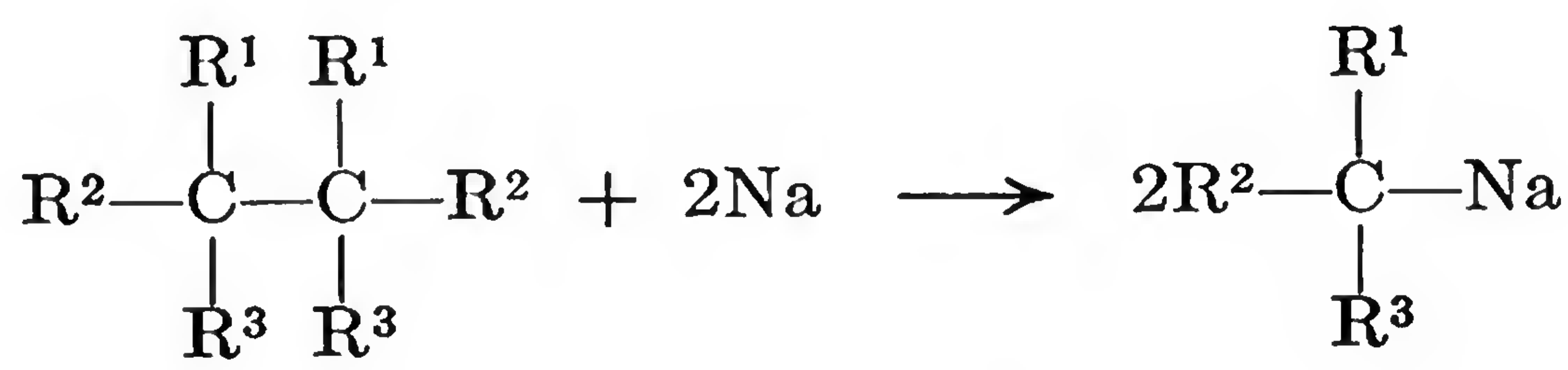
3-10-Dimethyl-3,10-diethyl-6,6,7,7-tetra-(3-methyl-3-ethylpent-1-yn-1-yl)-dodecadiyne-4,8 (*i.e.*, hexa-[3-methyl-3-ethylpent-1-yn-1-yl]-ethane), boiled for one hour in alcoholic solution, gave an isomer,[132] probably an analogous diallenyl with the structure of 3,14-dimethyl-3,14-diethyl-6,11-di-(3-methyl-3-ethylpent-1-yn-1-yl)-8,9-di-(3-methylpent-3-yl)-hexadecatetraene-6,7,9,10-diyne-4,12:



In the formation of the diallenyl products from the alkynyl hexa-substituted ethanes, there is an isomerization without hydrogen transfer. Apparently, a C—C *break,* and a C—C *union* of 2 *rearranged* free radicals occur as follows:

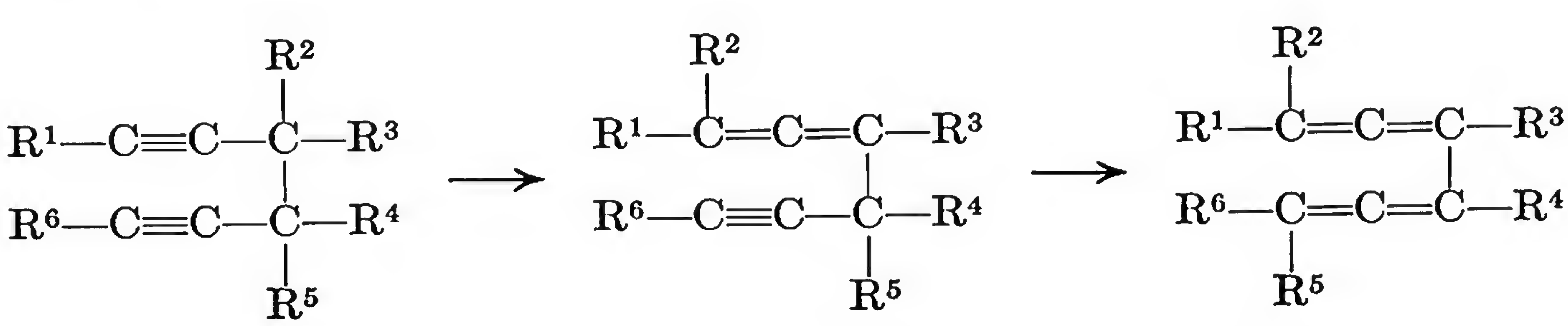


Such an explanation is supported by the observed formation of sodium alkyls upon treatment of the substituted ethanes with sodium amalgam.[564] An analogous type of reaction will be considered again in Chapter VI.

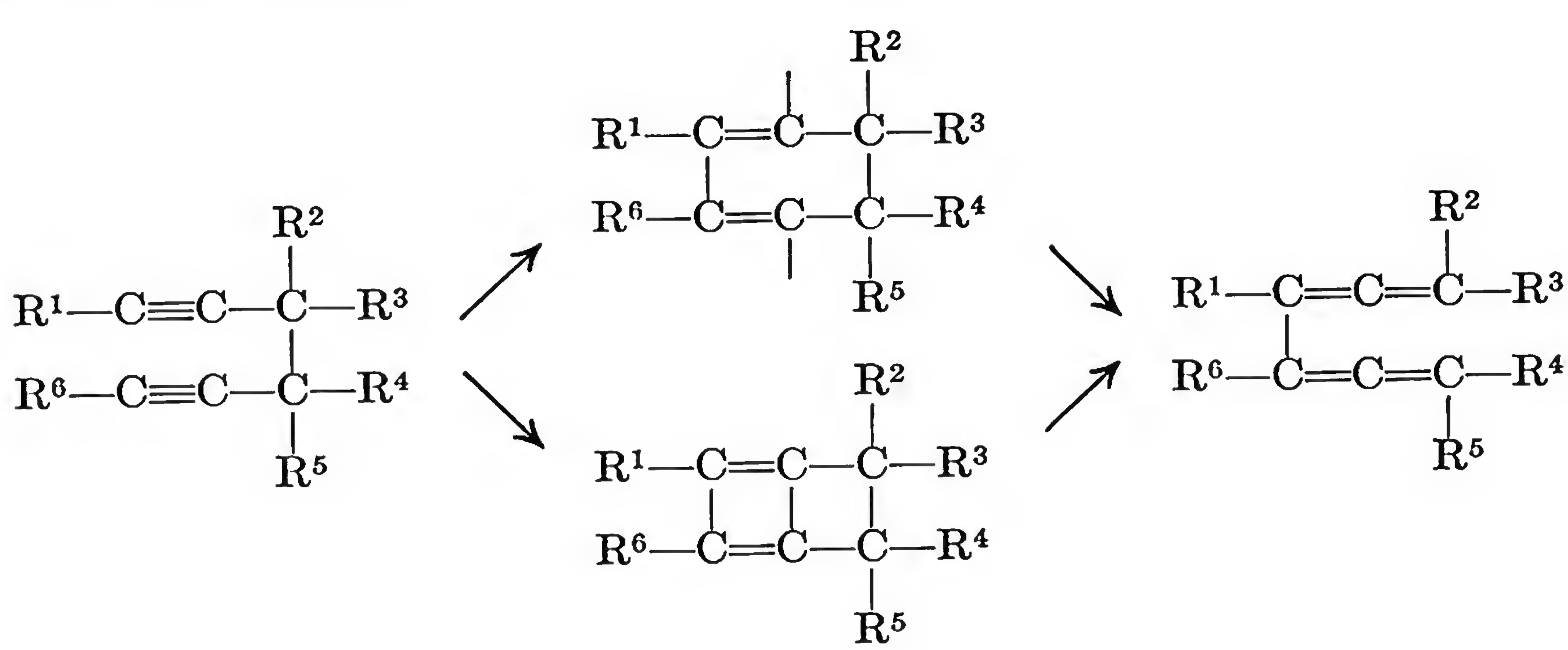


The isomerization mechanism in the alkynyl hexa-substituted ethanes could be clarified by investigating less symmetrical derivatives in the 4 following cases:

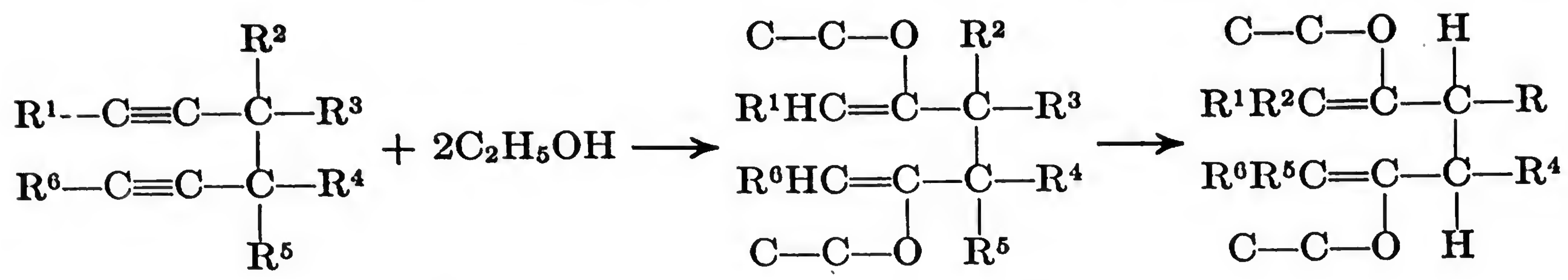
1. An intermediate allene-alkyne formation:



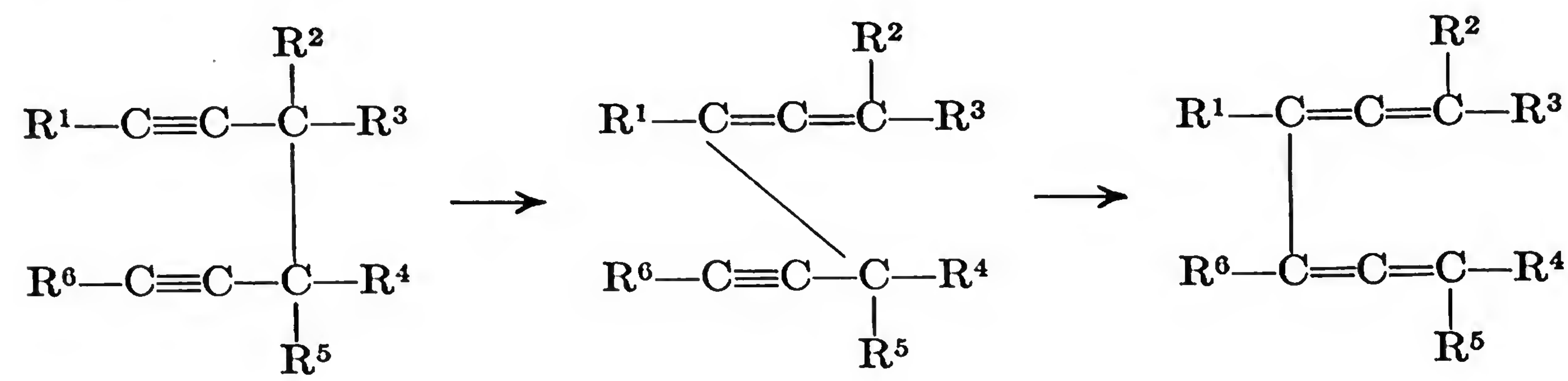
2. An intermediate cyclic- or bicyclic-compound formation:



3. A rearrangement of the two added hydrogen atoms and two R groups in alkenyl ethers:



4. A double "allylic type" of isomerization:[581]



The isomerizations of alkynes, alkadiynes, and alkapolyynes are given in Table 16, p. 284.

Conclusions

1. Isomerizations of alkynes take place only by a shift in position of the triple bond or by its transformation into two double bonds.

2. Alkynes form allenes when heated alone or in the presence of ethanol, alcoholic potash, "floridin," and pumice. Heating with alumina gives a conjugated diene.

3. Alkynes, H—C≡C—R, containing a tertiary third-carbon atom can isomerize up to, but not beyond, the allene stage. Alkynes containing a tertiary group *R* without a labile hydrogen (*i.e.*, a quaternary third-carbon atom) cannot isomerize at all by a hydrogen migration. Two labile hydrogens must be present on the third carbon-atom in order that triple bonds may shift "intact" and isomerize catalytically beyond the allene stage to new alkynes (in agreement with Faworsky's theory).

4. Sodium metal causes an alkyne-2 (methylacetylenes) to become an alkyne-1. Sodamide acts like sodium.* Both reactions probably depend upon a displacement of the equilibrium due to the formation of stable organosodium-compounds. "Floridin" converts an alkyne-2 into an alkyne-1 plus an allene; hence it is a catalyst of "mixed" type.

5. Alcoholic potash and soda-lime cause an alkyne-1 to become an alkyne-2. However, this change occurs at a higher temperature than the reverse isomerization.

6. Unconjugated alkadiynes form a conjugated system of triple bonds when treated with alcoholic potash. This isomerization shifts one

* Free sodium, present at times as an impurity,[98] may be responsible for the activity of sodamide.

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Chapter IV

Cyclanes, Spiranes, Bicyclanes, and Polycyclanes

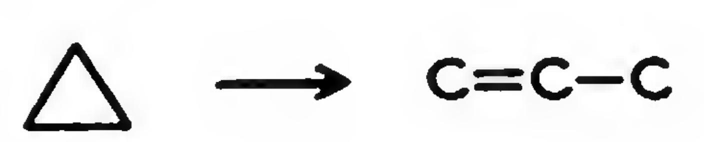
The cyclanes, spiranes, bicyclanes, and polycyclanes are discussed in the order: cyclanes and cyclanes with saturated side-chains, cyclanes with unsaturated side-chains, spiranes, bicyclanes and bicyclanes with saturated side-chains, bicyclanes with unsaturated side-chains, tricyclanes, and pentacyclanes. A tetracyclane has not been isomerized to date, although many interesting cases can be readily conceived.[353a]

Cyclanes and Cyclanes with Saturated Side-Chains

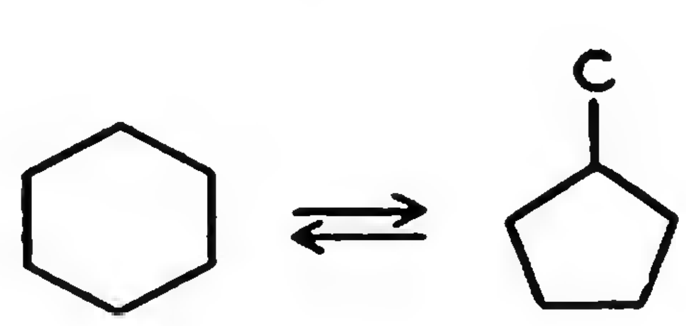
Mechanism

The isomerization of cyclanes (monocycloparaffins), with saturated side-chains or without side-chains, may proceed *theoretically* in 8 different directions:

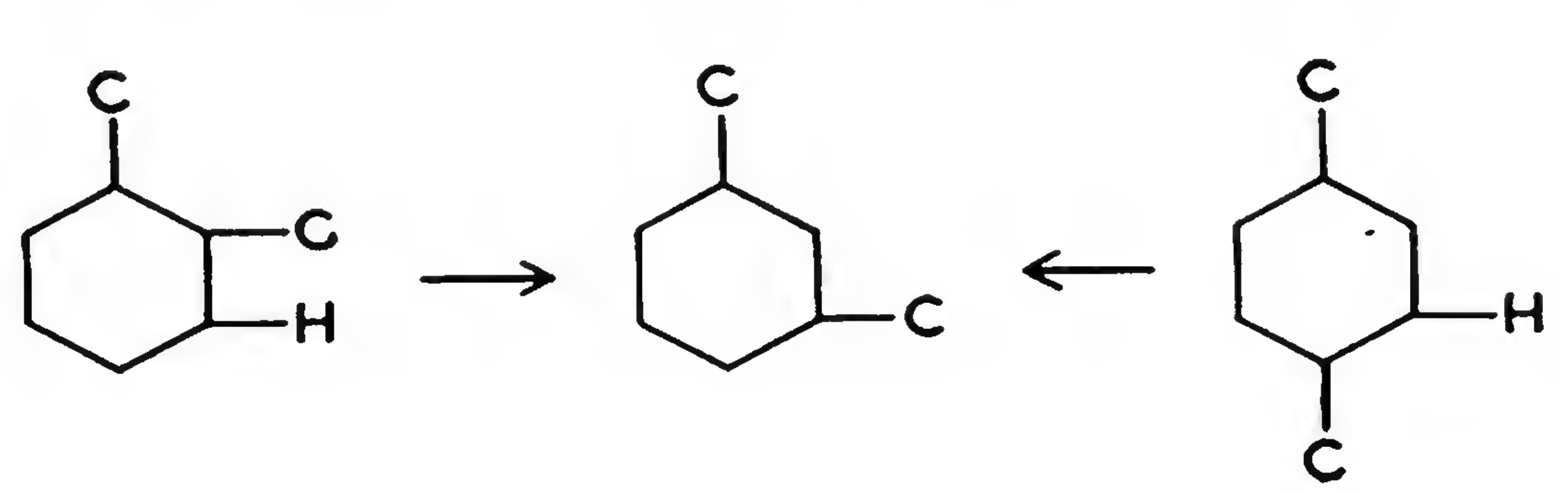
1. Rupture of the ring and formation of an alkene. This requires (over-all) a C—C and a C—H *break*, a C—C *union* to form a double bond, and a new C—H *tie*. This can be illustrated by the known reaction:



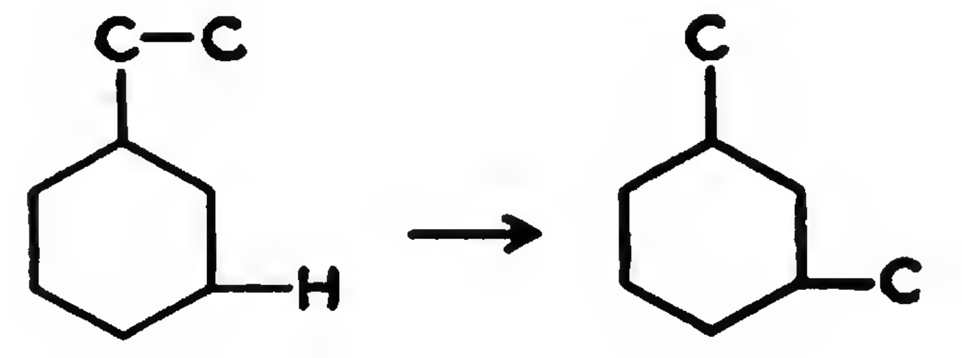
2. Change of the ring size. In its over-all aspect, this change requires a C—C and a C—H break, with subsequent recombination in new directions. This can be described by an established equilibrium:



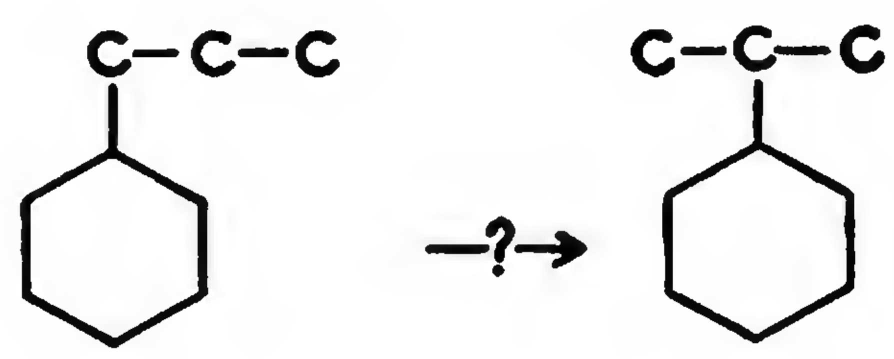
3. Shift of intact side-chains along the ring. This proceeds (over-all) by a dehydrogenation (one hydrogen atom only at the ring) plus dealkylation and a subsequent alkylation plus hydrogenation. An exchange in the position of alkyl and hydrogen occurs, as in the known reactions:



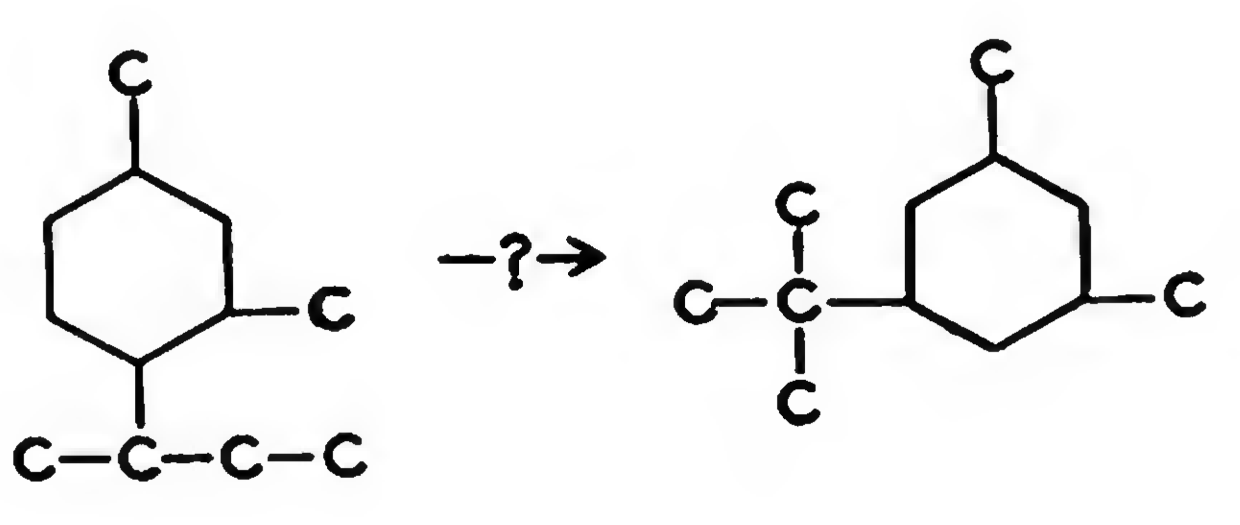
4. Isomerization by rupture within the side-chain, followed by an attachment of the one or more resulting new radicals along the ring. The over-all changes involved are dehydrogenation (usually of only one hydrogen atom at the ring) plus scission within the side-chain, followed by alkylation plus hydrogenation. The following observed reaction is characteristic of these changes:



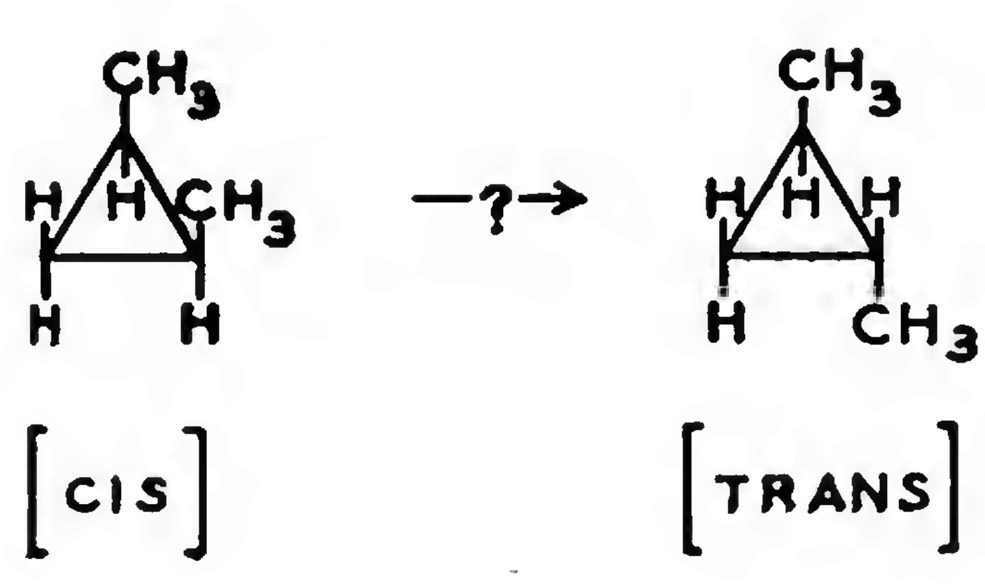
5. Isomerization of the side-chain itself, consisting of ruptures therein and the formation of a more symmetrical side-chain. This change has not been observed in the cyclanes to date.



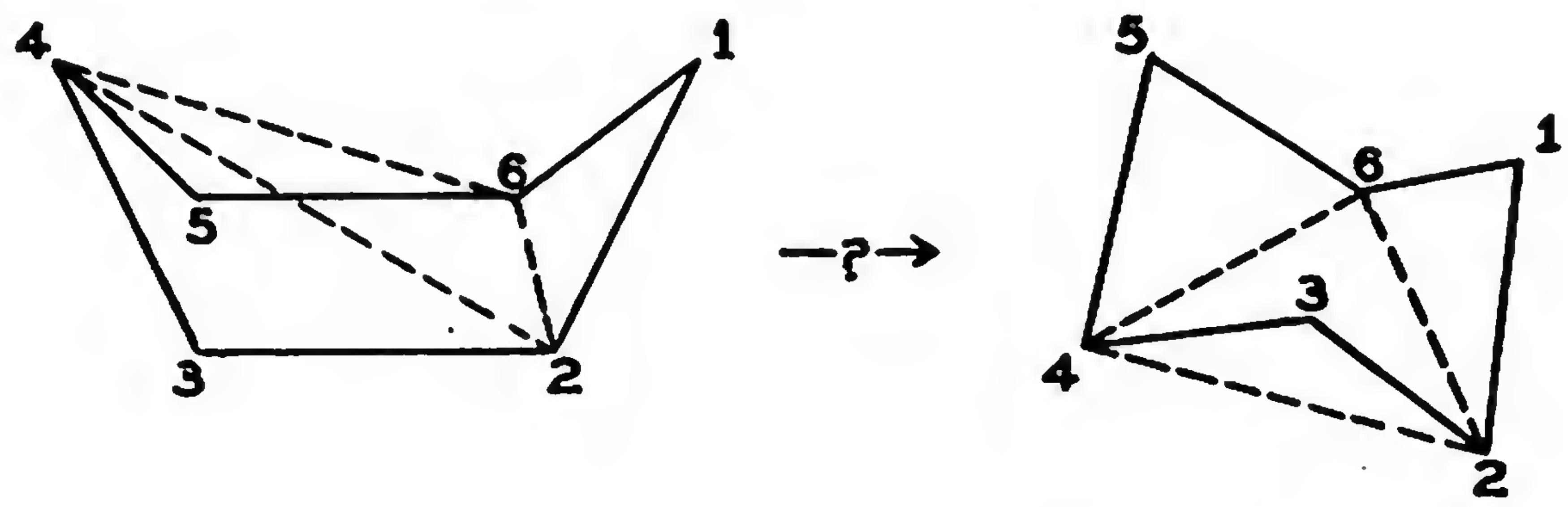
6. Isomerization by shifts of rearranged alkyl groups along the ring. The over-all changes are: (a) dehydrogenation (usually by displacement of only one hydrogen atom) plus dealkylation plus rearrangement of the alkyl; and (b) subsequent alkylation plus hydrogenation. These changes result in an exchange in position of hydrogen and new alkyl. This isomerization has not been observed in the cyclanes to date; it is a predictable combination of types 3 and 5.



7. *Cis-trans* or geometrical isomerization, *e.g.*,



8. Multiplanar isomerization, illustrated by the multiplanar forms of cyclohexane,



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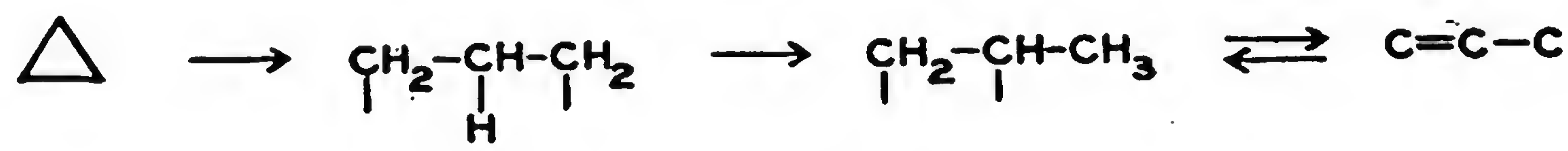
These reaction directions are merely illustrations of some of the types of isomerization that may be encountered among the cyclanes and their saturated homologs. Various combinations of directions are obviously possible.

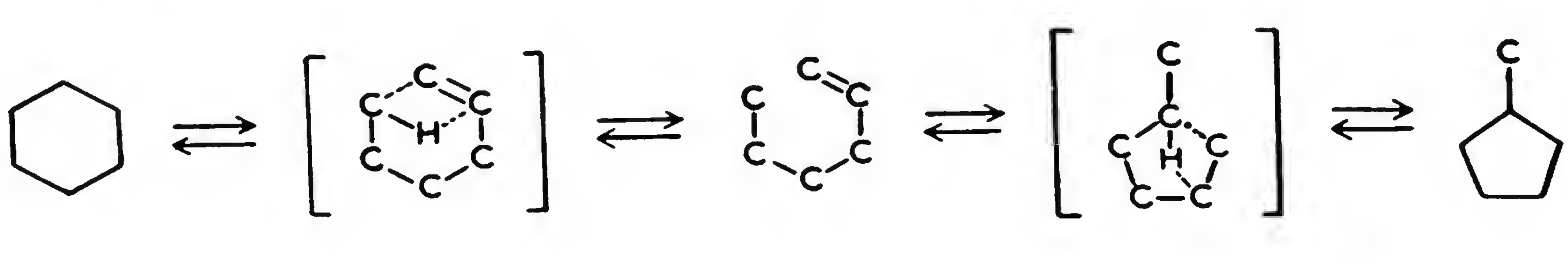
An isomerization of type 1 converts the monocyclic hydrocarbons into reactive alkenes. That of type 2 transforms certain rings into cyclohexanes, which in turn can be dehydrogenated to valuable aromatics. Types 3 and 4 are encountered often in synthetic organic chemistry, whereas types 7 and 8 are principally of theoretical interest. The first four of the 8 possible types have been observed experimentally and are well established.

Concerning the mechanism of these reactions, it should be noted that the first-two types of isomerization require ring rupture and shift of a hydrogen atom. Nef[396] formulated the isomerization of cyclopropane as follows:

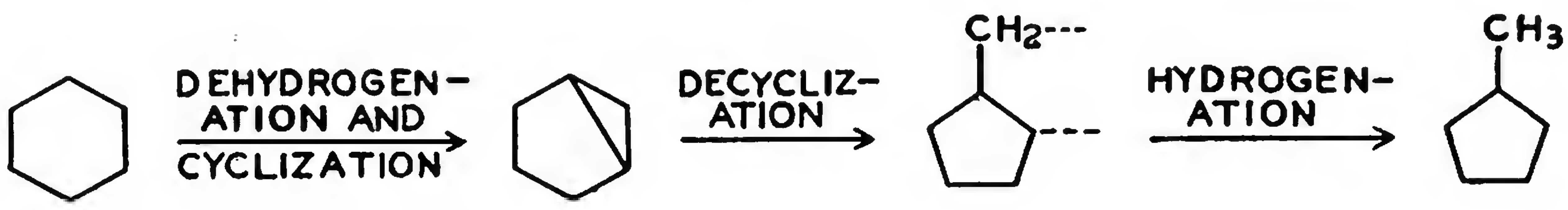


The formation of an "active trimethylene particle" and a scission of hydrogen from its central carbon atom were the essential changes elaborated upon for the isomerization. Schools of organic chemistry today emphasize the dependence of isomerizations on electronic transfer within the molecule,[641] rather than upon the formation of "active particles."

The role of catalyst may be that of a hydrogen carrier rather than an agent splitting C—C bonds. It should be recalled at this point that *dehydrogenating* catalysts were considered of especial importance in a mechanism of alkane isomerization involving hydrogen disproportionation. The actual C—C break within a ring may be a process proceeding through an intermediate active alkene, *e.g.*:

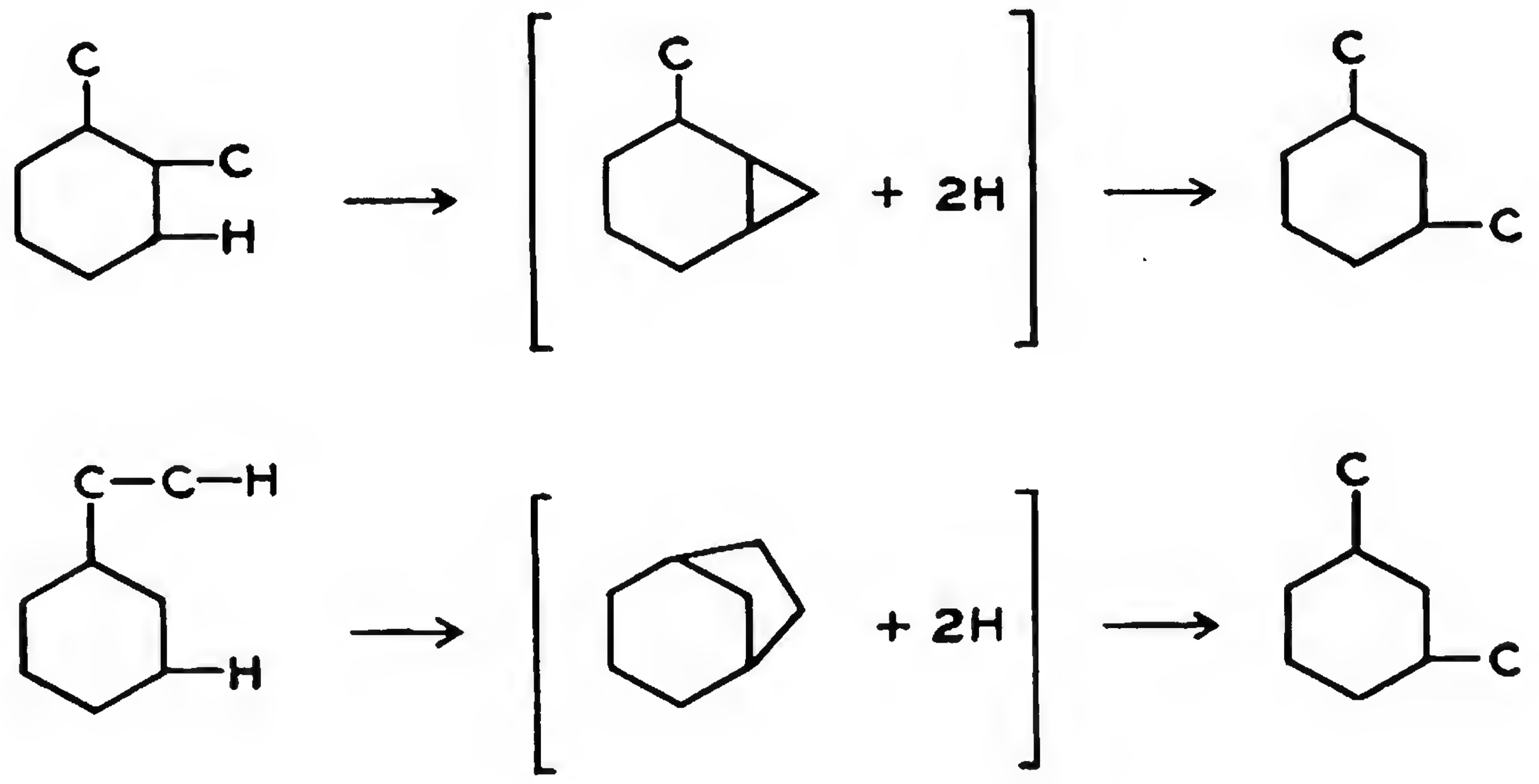


In isomerization type 2 (*i.e.*, change of ring size), still another mechanism may be considered, namely, dehydrogenation plus cyclization and successive decyclization plus hydrogenation:



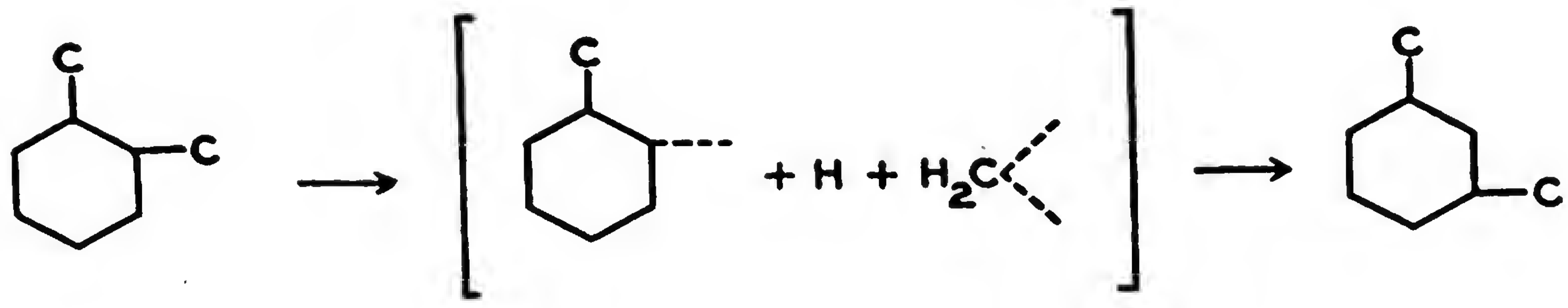
This mechanism was suggested for an acetylation reaction using cyclohexane[602] and for an isomerization of the same hydrocarbon.[675] Such inter- and intramolecular hydrogenation plus dehydrogenations in the presence of aluminum halide catalysts have been observed in numerous cases.[195, 280, 281, 523, 524] The free radical, cyclohexyl, may isomerize into methylcyclopentyl in the related reaction of cyclohexane with acetyl chloride and aluminum chloride.[398] This mechanism is not in conflict with a dehydrogenation plus cyclization as followed by decyclization plus hydrogenation. It has been pointed out that like electrical charges may be responsible for ring expansions.[406] The latter are attributed to like electrical charges in 2 adjacent ring-carbon atoms, especially if enhanced by similar charges in side-chains attached to each of these carbons. Unlike electrical charges in side-chains, according to this viewpoint, would favor ring contraction. As already pointed out, "cyclic intermediates" can be considered as a mobile system of diyl forms that seldom attains the bicyclic, "intermediate" state of transformation illustrated herein.

Isomerization types 3 and 4 proceed, as in the case of alkanes, by "migrations" of hydrogen atoms and alkyls. A particular but unproved mechanism would be the formation of a bicyclic intermediate. A temporary closure of side-chain upon the ring, via dehydrogenation, followed by a hydrogenation and decyclization, describes this mechanism:



A simpler isomerization via alkylidene groups (such as methylene), or via an alkene of alkylation, is conceivable upon admission of dehydro-

genation and decyclization ("the C—C break") as parts of the isomerization mechanism:



Isomerization types 5 and 6, with rearrangement of the side-chain itself, are not encountered because of a distribution of small new radicals along the ring (type 4). Isomerization type 7 (*cis-trans*) among the cyclanes has remained almost unobserved to date, although it is recognized that cyclic structures restrict the freedom of rotation of alkyl groups about the carbon atoms of rings.[213] Type 8, involving nonplanar rings, will be considered in the isomerization of cyclohexanes.

Isomerizations

Cyclopropanes. The isomerization of cyclopropane into propene, in contrast with the opposite reaction, is one of the easy isomerizations in hydrocarbon chemistry. Passage of cyclopropane through a glowing glass tube gave propene.[576] While only 1-2 per cent of propene is formed at 370° in the absence of a catalyst and with long contact time,[279] the reaction can be almost complete at 550° [62] or 600°.[590] Tubes of quartz are preferable to those of glazed or unglazed porcelain, since the former reduce polymerization.[590]

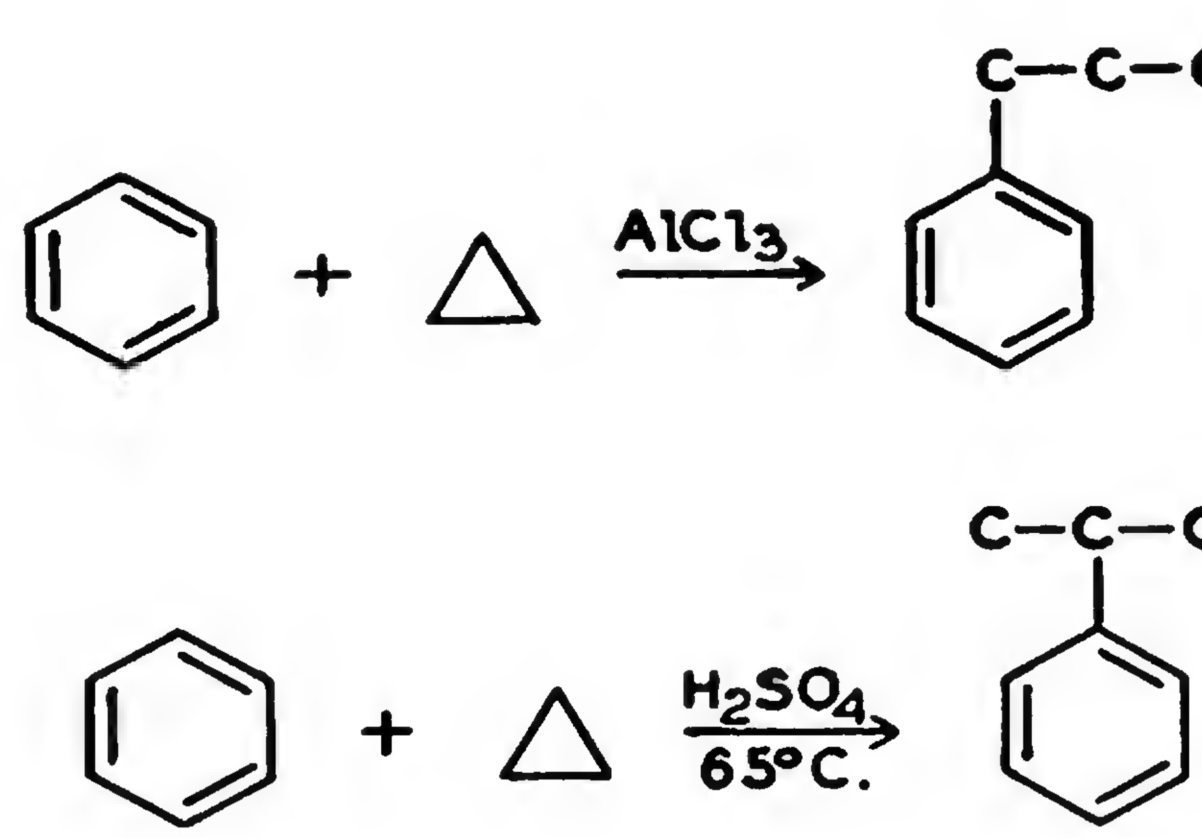
A kinetic study [104] of the reaction at 500° showed that the isomerization of cyclopropane is unimolecular, with an activation energy of 65.0 kilocalories per gram-mole. The propene yield was 25-65 per cent. The reaction-velocity constants are in agreement with a rate-determining step consisting of a hydrogen migration.[465] Earlier workers [590] found 63.9 kilocalories per gram-mole for the heat of activation at 550-650°, and pointed out that the isomerization of cyclopropane is the first example of a monomolecular reaction among gases. From heat of combustion data for propene [476] and cyclopropane,[224] it can be demonstrated that the exothermic heat of isomerization of cyclopropane into propene, at 25° and one atmosphere pressure, is about 4.8 kilocalories per gram-mole. This large energy liberation is due to the highly-strained condition of the cyclopropane ring.

The use of catalysts greatly reduces the temperature and time required for the formation of a given percentage of propene in the final product. Thus, cyclopropane in the presence of platinum black, air, and moisture gave 19-30 per cent of propene in 5 months at room temperature.[577] At

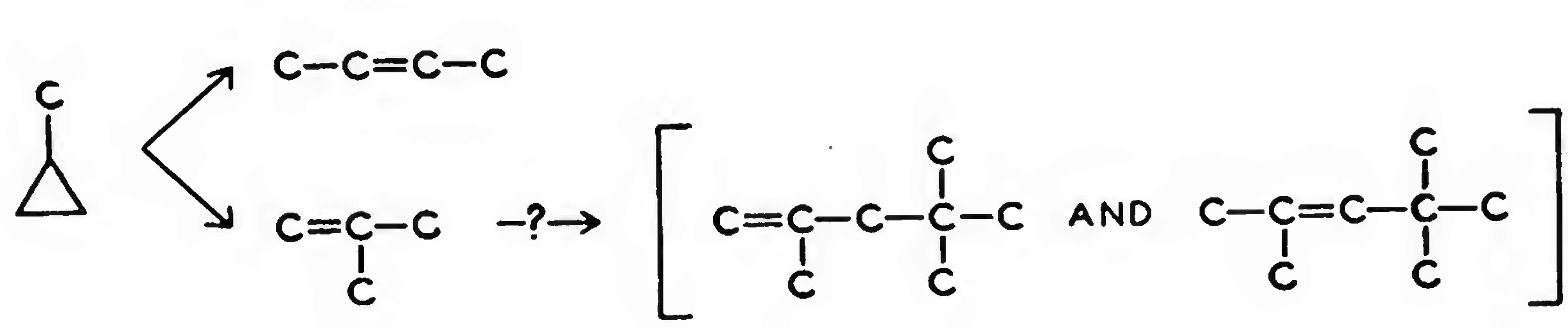
100° the conversion is 45 per cent in 120 hours, against 15-18 per cent without catalyst.[577] Passage of cyclopropane over a platinum black catalyst (Levy's) at 200° and 315° gave 4.5 and 29 per cent of propene, respectively.[279] Platinum black and platinized asbestos at 400° yielded up to 70 per cent of propene.[472]

Cyclopropane, passed over iron filings at 600°, gave 50-70 per cent of propene.[270, 273] Passage of cyclopropane over alumina at 350-360° and 370-385° yielded 15 and 20 per cent of propene respectively.[279] Iodine vapor at 279° is also a catalyst, but the main reaction is iodination to 1,3-diiodopropane.[426]

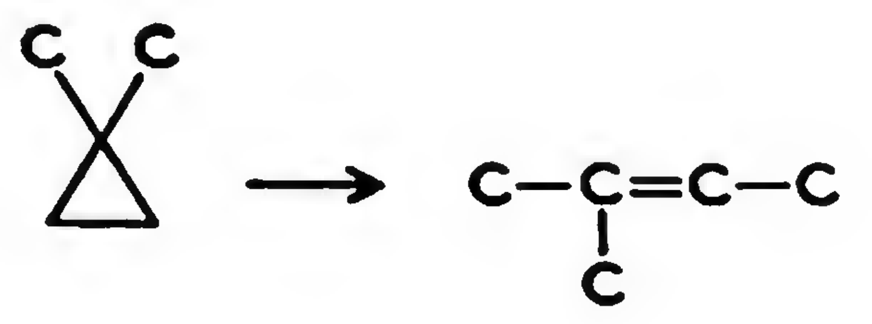
Isomerization of cyclopropane to propene (in the presence of 80-per cent sulfuric acid at 65°) is probably an intermediate step in the alkylation of benzene, since isopropylbenzene is formed instead of *n*-propylbenzene.[287] Milder conditions, such as sulfuric acid at 0° or aluminum chloride at 71°, gave only *n*-propylbenzene, which may be considered the normal product from cyclopropane. These alkylations in the presence of sulfuric acid may involve the intermediate formations of *n*-propyl and isopropyl hydrogen sulfates.[287] The last ester cannot be formed directly and, if present, would represent an isomerization either of cyclopropane into propene, or of *n*-propyl into isopropyl hydrogen sulfate.



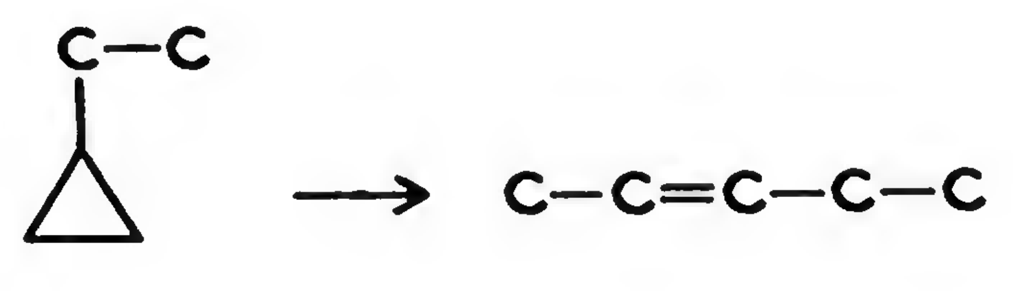
The alkyl derivatives of cyclopropane are also readily isomerized to alkenes, due to the presence of the highly-strained cyclopropane ring. Methylcyclopropane isomerized into butene-2 and some isobutene, and partly polymerized, in the presence of alumina at 340-360°.[140] The decyclization of methylcyclopropane into isobutene is given as an explanation of the dehydration of butanol-2 into isobutene (at 450° in a copper tube containing either alumina or zinc chloride).[288]



1,1-Dimethylcyclopropane formed 92 per cent of 2-methylbutene-2 (trimethylethylene) in the presence of alumina at 340-345°:[279]

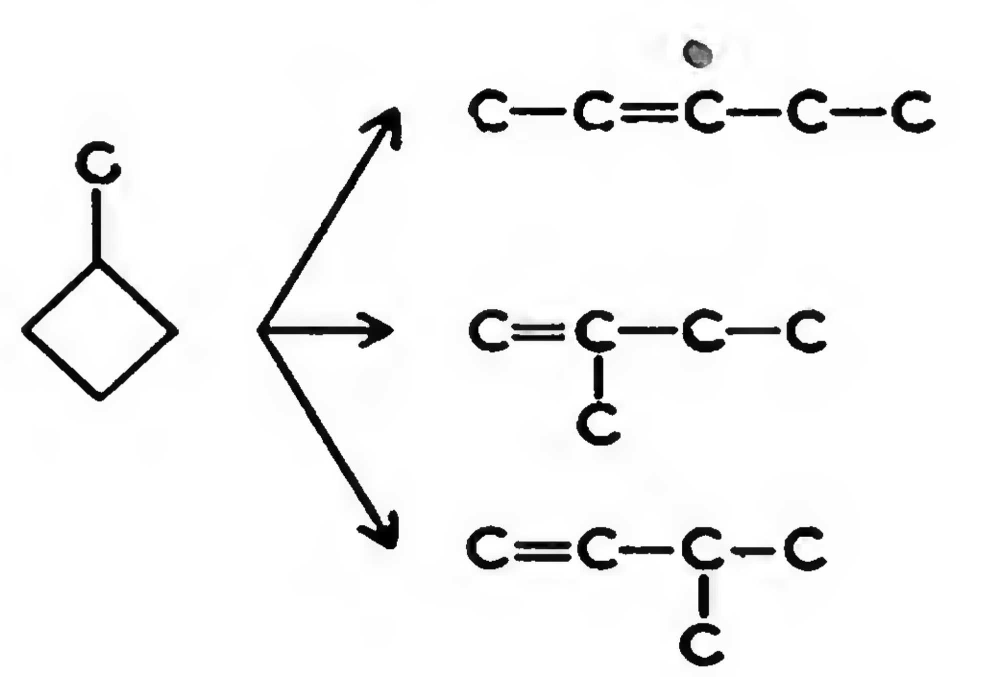


Ethylcyclopropane yielded pentene-2 when passed over alumina-asbestos at 300-310°:[479]



Cyclobutanes. No experimental work has been reported on the direct isomerization of cyclobutane into a butene. Thermodynamically, the reaction should proceed to a lesser extent at a given temperature than the corresponding change of cyclopropane into propene.

Methylcyclobutane isomerized over alumina at 400° into pentene-2, 2-methylbutene-1, and 3-methylbutene-1, which apparently shows that ring rupture occurs in either of the two possible places:[480]



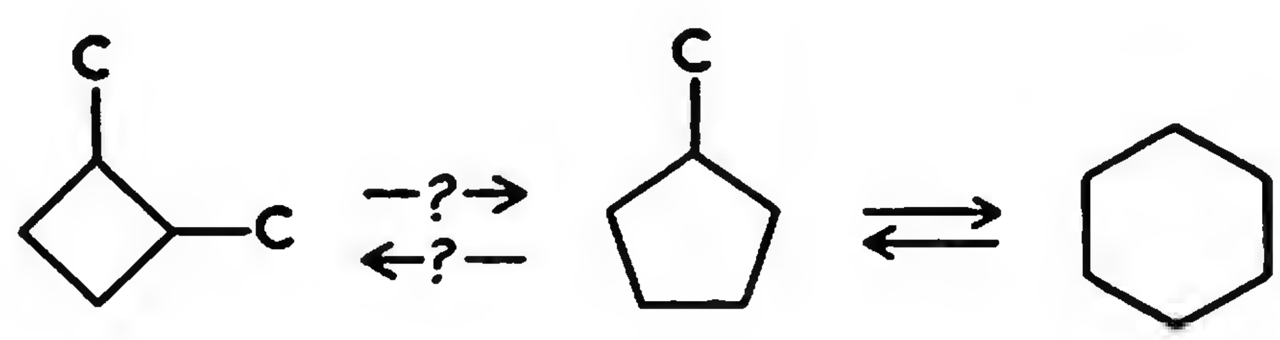
A study of the rates of formation and possible interconversion of the three resulting isomers seems desirable.

Cyclopentanes. With rings containing five or more carbon atoms, a cyclane isomerization of type 2 (change of the ring structure) takes place. However, there is some indication that an isomerization of type 1 (decyclization) also occurs.

An isomerization of cyclopentane has not been observed to date. Cyclopentane remained unchanged when heated under reflux for 8 hours with anhydrous aluminum chloride.[129]

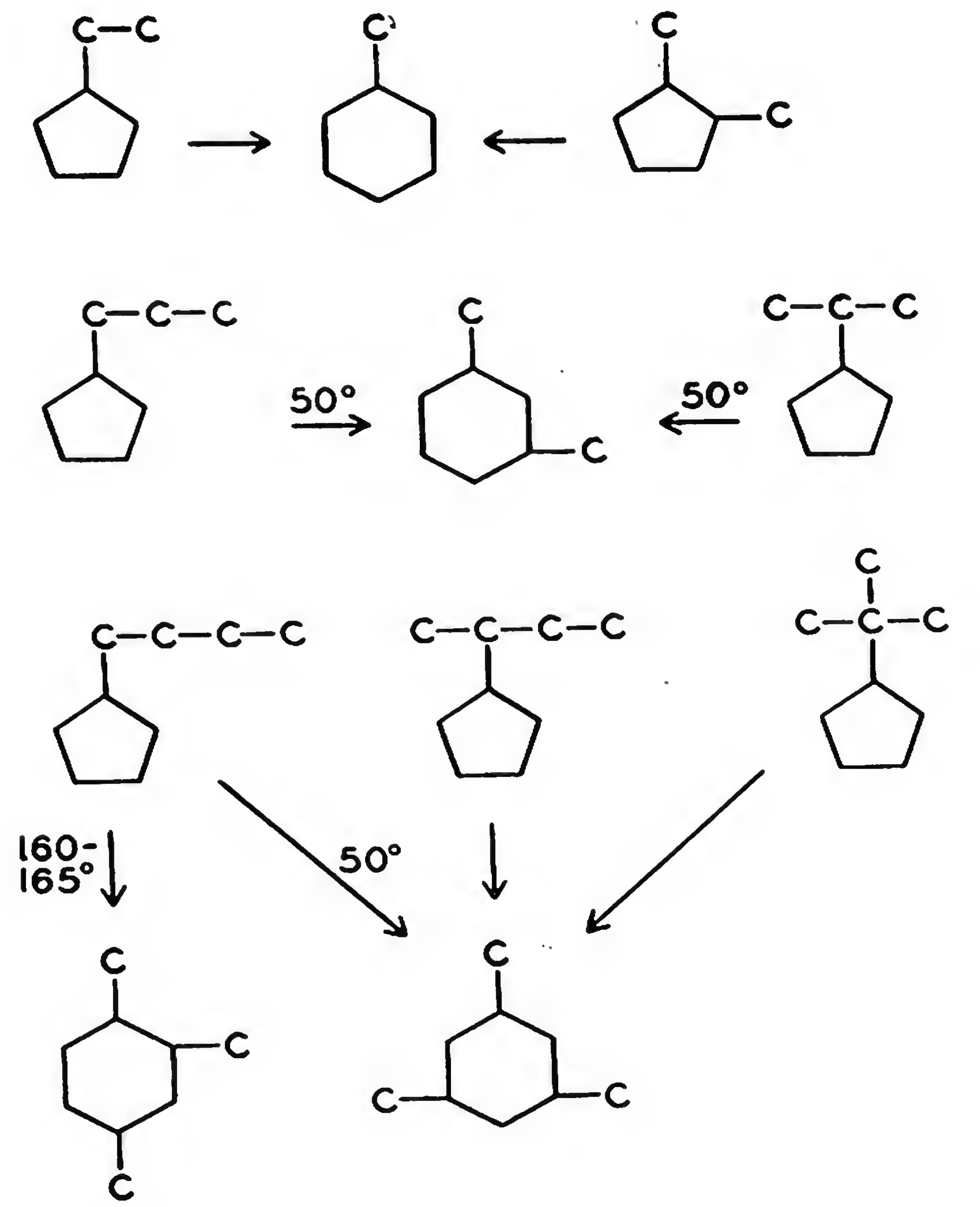
Methylcyclopentane, heated under reflux for 30 hours with aluminum chloride (30.5 per cent) plus water (0.8 per cent), underwent a reversible type 2 isomerization (change of ring size), forming an "equilibrium mix-

ture" containing 22.8 per cent of methylcyclopentane and 77.2 per cent of cyclohexane.[399] Heated under reflux for 3 hours with aluminum chloride (20.9 per cent) and water (0.7 per cent), methylcyclopentane gave cyclohexane (58.6 per cent) and low- and high-boiling products.[215] It seems probable that methylcyclopentane when treated with a large amount of aluminum bromide gives also some 1,2-dimethylcyclobutane.[675] Anhydrous aluminum chloride is reported to be also a catalyst.[595] Compositions of the "equilibrium mixture" are dependent upon reaction temperatures. *Prior* to the occurrence of side reactions, these compositions at 25.1°, 61.0°, and 99.5° are respectively 12, 21.5, and 46 per cent of methylcyclopentane and 88, 78.5, and 54 per cent of cyclohexane.[441] "Equilibrium mixtures" prepared at 20° and 80° were found to contain respectively 11.0 and 23.4 per cent of methylcyclopentane and 88.0 and 76.6 per cent of cyclohexane.[529a] Methylcyclopentane, heated at 500° with sulfur compounds of cobalt and of molybdenum under 100 atmospheres' initial hydrogen pressure, formed a small amount of cyclohexane:[452]



Recent work on the isomerization of alkylcyclopentanes reports yields of over 80 per cent of isomeric cyclohexanes (when the former are heated for 18 hours at 50° with 13 mole per cent of aluminum chloride and a trace of water).[440] In this work, ethylcyclopentane gave methylcyclohexane; propyl and isopropyl cyclopentanes formed 1,3-dimethylcyclohexane, whereas *n*-, *sec*-, and *tert*-butyl cyclopentanes gave 1,3,5-trimethylcyclohexane. Side reactions were reported absent. However, treatment of propylcyclopentane with aluminum chloride at the elevated temperature of 140-145° gave 1,3- and 1,4-dimethylcyclohexanes and alkanes.[598] Ethylcyclopentane yielded 83.4 per cent of methylcyclohexane, along with 2.6 per cent of unchanged hydrocarbon, when treated 20 hours at 110-115° with aluminum chloride.[597] Isopropylcyclopentane yielded about 70 per cent of 1,3- and 1,4-dimethylcyclohexanes, along with 17 per cent of alkanes and substituted cyclopentanes, in an isomerization effected by aluminum chloride at 125-130°.[598a] *n*-Butylcyclopentane formed a considerable amount of 1,2,4-trimethylcyclohexane and 5.7 per cent of alkanes, upon treatment for 20-24 hours at 160-165° with aluminum chloride.[596] *n*-Amylcyclopentane yielded 55 per cent of "inseparable" cyclohexane derivatives, probably tetramethylcyclohexanes, and some low-boiling and high-boiling hydrocarbons when subjected to the action of aluminum chloride at 150-155° for 20 hours.[598b]

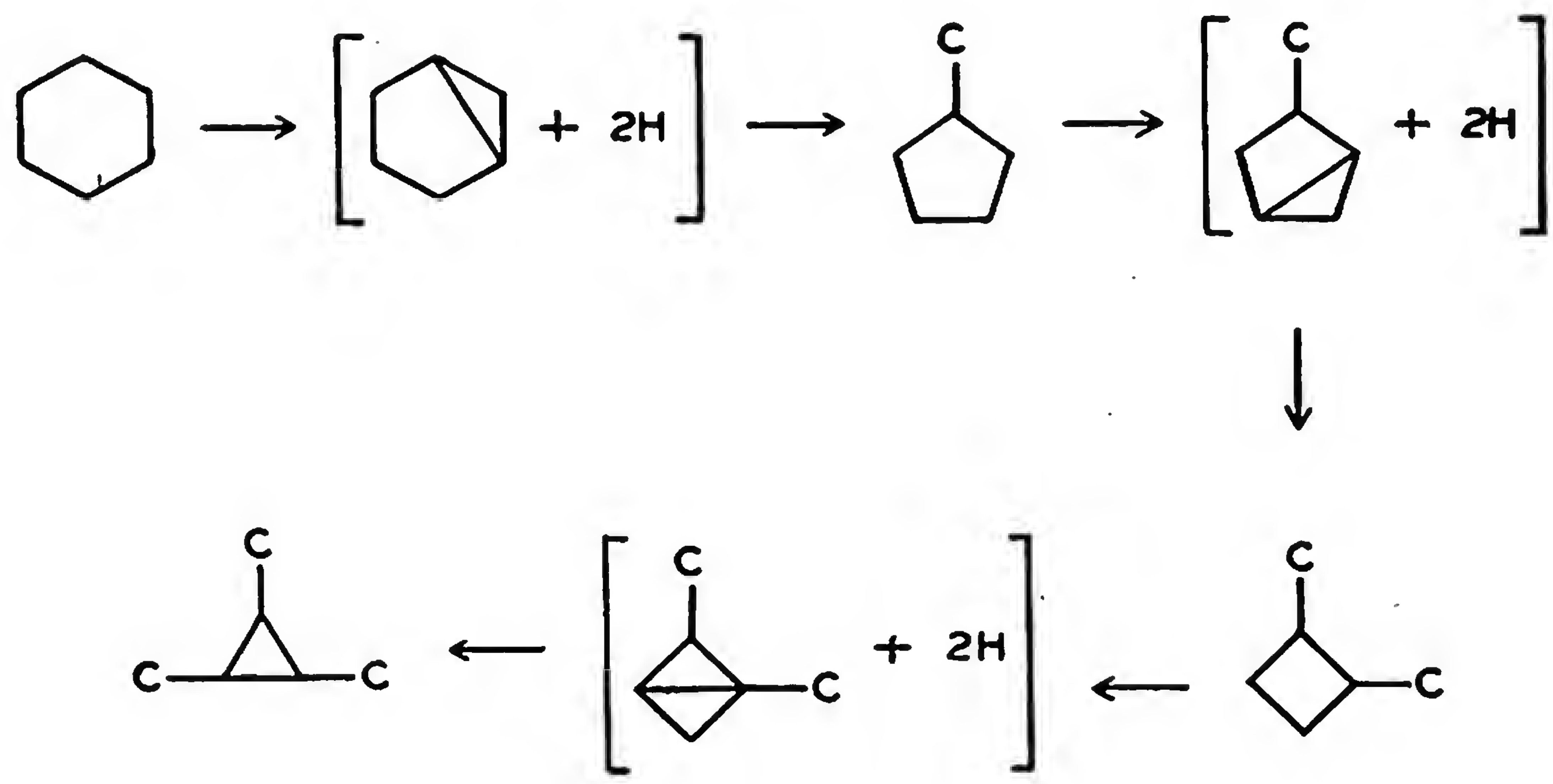
1,2-Dimethylcyclopentane was isomerized to 96.7 per cent of methylcyclohexane in the presence of aluminum chloride at 100-104°.[598c]



Cyclohexanes. The partial isomerization of cyclohexane to methylcyclopentane, which is a reaction with an interesting history, was first observed in 1902. When cyclohexane was heated at 330° in a potash-glass tube, the reaction was catalytic; a soda-glass tube gave negative results.[16] Cyclohexane, treated with aluminum chloride for 48 hours at room temperature and afterwards heated to the boiling point, formed hydrogen chloride gas, some methylcyclopentane, and a large amount of resins.[16] Considerable cyclohexane was also recovered.

In later work (1911), cyclohexane was heated with alumina (6.98 per cent) for 4 hours at 500-510° and 110-120 atmospheres' pressure, forming a small amount of methylcyclopentane, besides hydrogen, methane, and other hydrocarbons.[275] In 1927, cyclohexane, when heated 3 days at 420° in an alkali-glass tube, gave 5 per cent of methylcyclopentane.[547] Cyclohexane was treated (1929) with aluminum bromide (25 mole per cent) for 12 hours at 180°; this resulted in only a slight change.[674] Later work [675] showed that cyclohexane when heated for 24 hours on a water bath with aluminum bromide (51.4 per cent) forms two fractions. One of these with b.p. of 78-80° was taken to be a "stable form" of cyclohexane, whereas the other (3.57 per cent) was stated to be dimethycyclo-

butane. It was also claimed that aluminum chloride gives about the same results as aluminum bromide. The last catalyst was considered to catalyze the following sequence of reactions:



Apparently the action of aluminum bromide does not stop with the formation of methylcyclopentane, but goes on to form dimethylcyclobutane, trimethylcyclopropane, and probably alkanes.[675]

Cyclohexane, in 1933, was heated under reflux for 3 hours with aluminum chloride (29.8 per cent) plus water (0.8 per cent), giving methylcyclopentane (5 per cent), unaltered cyclohexane, and probably some *n*-hexane.[399] Dimethylcyclobutane was not obtained as a product, and the reported equilibrium mixture for the reflux temperature consisted of methylcyclopentane (22.8 per cent) and cyclohexane (77.2 per cent). In the following year, an investigation[280] was carried out with cyclohexane and aluminum chloride (9.77 per cent) in the presence of hydrogen chloride for 24 hours at 150°. The reaction products were hydrogen, isobutane (1327 cc. per 307.4 g. cyclohexane), methylcyclopentane, some unchanged cyclohexane, 1,3-dimethylcyclohexane (6.5 per cent), dimethyldicyclopentyl (9 per cent), and dicyclohexyl (3 per cent). The combined mixture of methylcyclopentane and unchanged cyclohexane accounted for only 60 per cent of the original cyclohexane. A yield of 16.0 per cent of methylcyclopentane was obtained in the treatment of cyclohexane with aluminum chloride and some water.[215] The experimental conditions were incompletely disclosed, but the products also included isohexanes, 1,3-dimethylcyclohexane, dimethyldicyclopentyl, dicyclohexyl, and some unreacted cyclohexane. These side products are some of those reported previously.[280] The composition of the "equilibrium mixture" or distillate is highly dependent upon temperature. The "equilibrium amount" of methylcyclopentane steadily increases with any rise in reaction temperature until, at 140°, it reaches that of the cyclohexane.[529a] The compositions for equilibrium conditions at 25.1°, 61.0°, and 99.5°,

in the presence of either partially hydrated aluminum chloride or aluminum bromide with hydrogen bromide, were mentioned in the discussions on methylcyclopentane.[441]

The isomerization of cyclohexane into methylcyclopentane is an interesting reaction from the thermodynamic standpoint, since energy must be added or absorbed from the surroundings of the molecules. The endothermic heat of isomerization of cyclohexane into methylcyclopentane is 3.83, or 7.30 kilocalories per gram-mole (for the temperature ranges 25.1°-61° and 61°-99.5°, respectively.[441] Other values for the heat of isomerization of cyclohexane into methylcyclopentane are 3.51 and 3.93 kilocalories per gram-mole at 25°, obtained respectively from equilibrium measurements [215] and from new values of the heats of combustion of these hydrocarbons.[386] The corresponding free energy changes are 1.15 kilocalories [215] and 0.95 kilocalories [386] per gram-mole.

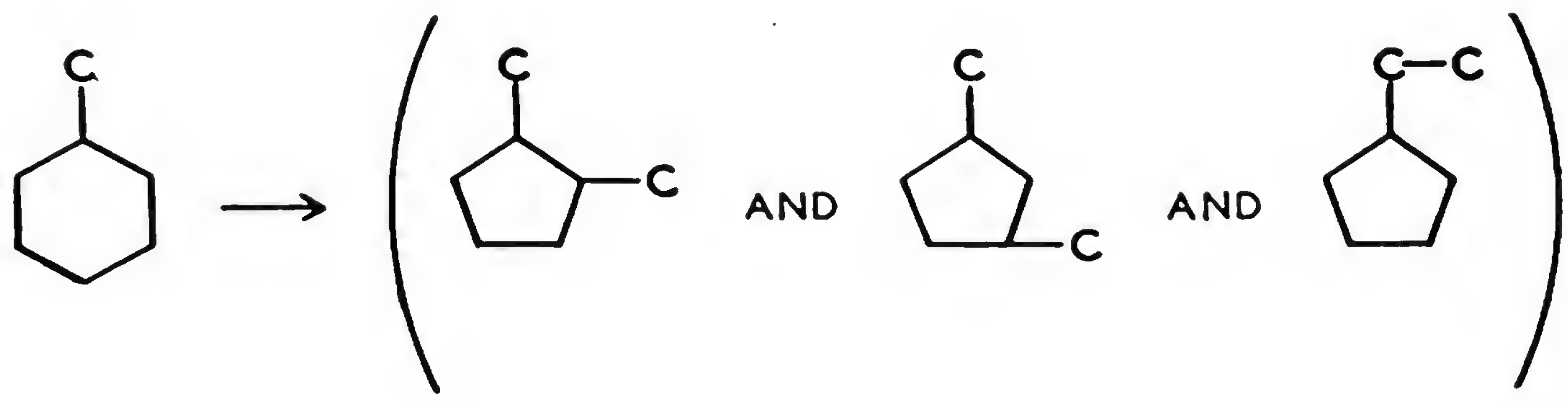
Recent work has demonstrated that the yield of methylcyclopentane can be increased by use of other catalysts. Cyclohexane heated at 400° under 140-350 atmospheres' pressure of hydrogen in the presence of molybdenum disulfide (MoS_2) gave a considerable amount of methylcyclopentane (62 per cent of the *recovered* hydrocarbons), together with *n*-hexane and isohexanes.[454] Gases, unsaturated hydrocarbons, and aromatics developed as additional products at 500°.[453b] A practically complete isomerization of cyclohexane into methylcyclopentane occurred in one hour at 500° under 100 atmospheres' initial pressure of hydrogen in the presence of sulfur compounds of cobalt and of molybdenum.[452] Cyclohexane formed 67.7 per cent of methylcyclopentane, together with 0.6 per cent of aromatics, when passed at 411° and 200 atmospheres' hydrogen pressure over Japanese acid clay supporting molybdenum sulfide.[4] A mechanical mixture of molybdenum trioxide and sulfur proved less active as a catalyst, resulting in only 10.9 per cent of methylcyclopentane at 439° and 262 atmospheres' hydrogen pressure.[5] The yield was increased to 15.3 per cent by simultaneously halving the time of treatment and slightly lowering the reaction temperature and pressure.[5, 5a] The use of a catalyst composed of molybdenum sulfide, supported upon a Japanese acid clay that was previously activated by mineral acids, was effective in forming 17.2 per cent of methylcyclopentane under the foregoing, less-drastic, reaction conditions.[5a]

Methylcyclohexane occurs in stable and unstable forms, which are possibly the multiplanar "C" and "Z" molecules demanded by the Mohr [378] and Sachse [498] theory. Stable methylcyclohexane (b.p. 100.4-100.7°/773 mm. Hg, $D_4^{20} = 0.7704$, $n_D^{20} = 1.42410$) was prepared by: (1) hydrogenation of certain methylcyclohexenes (via phosphorus pentoxide on 1-, 3-, or 4-methylcyclohexanols), or (2) the aging for 7 days,

or heating to 40-60°, of unstable methylcyclohexane (b.p. 100.2-100.4°/768 mm. Hg, $D_4^{20} = 0.7679$, $n_D^{20} = 1.42306$) (via hydrogenation of the methylcyclohexene from 2-methylcyclohexanol and phosphorus pentoxide).[611] This is the first experimental evidence for an isomerization involving the multiplanar structure of the cyclohexane hydrocarbons. The validity of this work has been questioned[644] and answered.[612] The dehydration of 2-methylcyclohexanol and hydrogenation of methylcyclohexenes were investigated subsequently, although without definite evidence for or against multiplanar structure.[446] Typical preparations of the unstable form of methylcyclohexane (b.p. 100.4°/763 mm. Hg, $D_4^{20}=0.7678$, $n_D^{20}=1.42306$; b.p. 100.5°/764 mm. Hg, $D_4^{20}=0.7676$, $n_D^{20} = 1.42311$) resulted from the heating of 2- and 4-methylcyclohexanone semicarbazones with sodium ethoxide.[128] These preparations, upon standing for several days, formed stable methylcyclohexane (b.p.?, $D_4^{20} = 0.7694$, $n_D^{20} = 1.42321$; b.p. 100.4°/758 mm. Hg, $D_4^{20} = 0.7695$, $n_D^{20} = 1.42326$). According to the last experiments, the density and refractive index of the stable form are only slightly higher than that of the unstable one. Theoretically, the multiplanar "C" form should be very mobile, since a continuous series of tensionless positions is available for the molecule.[111]

Methylcyclohexane, when heated with aluminum bromide, was recovered unchanged.[674] The reaction conditions were not stated. Methylcyclohexane did not isomerize when treated with aluminum chloride (25 per cent) at 140-150°.[571] On the other hand, heating of methylcyclohexane under reflux for 10 hours with aluminum chloride (25 per cent) gave a trace of (*cis* + *trans*)-1,2-dimethylcyclopentane (0.003 per cent), 2-3 per cent of combined gases (hydrocarbons, mostly isobutane) and polymers, together with much methylcyclohexane.[400] Methylcyclohexane yielded 5.4 per cent of ethylcyclopentane, along with 80.9 per cent of unchanged hydrocarbon, when treated 20 hours at 110-115° with aluminum chloride.[597] Recently, methylcyclohexane was heated at 80° under pressure for 10 hours with 5 per cent each of aluminum chloride and hydrogen chloride.[529a] This treatment resulted in the formation of about 3.5 volume-per cent of total *trans*-1,2- and *trans*-1,3-dimethylcyclopentanes, along with a little cyclohexane.

Methylcyclohexane, when reacted in the presence of molybdenum disulfide (MoS_2) for 26 hours at 400° under 350 atmospheres' pressure of hydrogen, gave 50 per cent of combined 1,2- and 1,3-dimethylcyclopentanes, together with a trace of ethylcyclopentane, and some alkanes, principally of iso- structure.[455] There was no formation of 1,1-dimethylcyclopentane:



Isomerizations of types 3 and 4, involving side-chains of the cyclohexane homologs, take place in the presence of aluminum chloride. 1,1-Dimethylcyclohexane yields 1,2-, 1,3-, and 1,4-dimethylcyclohexanes when isomerized at 80° with 5 per cent of aluminum chloride and 15 per cent of hydrogen chloride under pressure.[529a] Ortho and para dimethyl derivatives isomerize to meta compounds, but ethyl-substituted cyclohexane gives the corresponding methyl derivatives. The following set of isomerizations has been observed: [228, 571]

(1) 1,3-Dimethylcyclohexane from either 1,2- or 1,4-dimethylcyclohexane treated for 7 hours at 115-120° with aluminum chloride (23 per cent).

(2) 1,3-Dimethylcyclohexane from ethylcyclohexane heated for 8 hours at 115-120° with aluminum chloride (21 per cent).

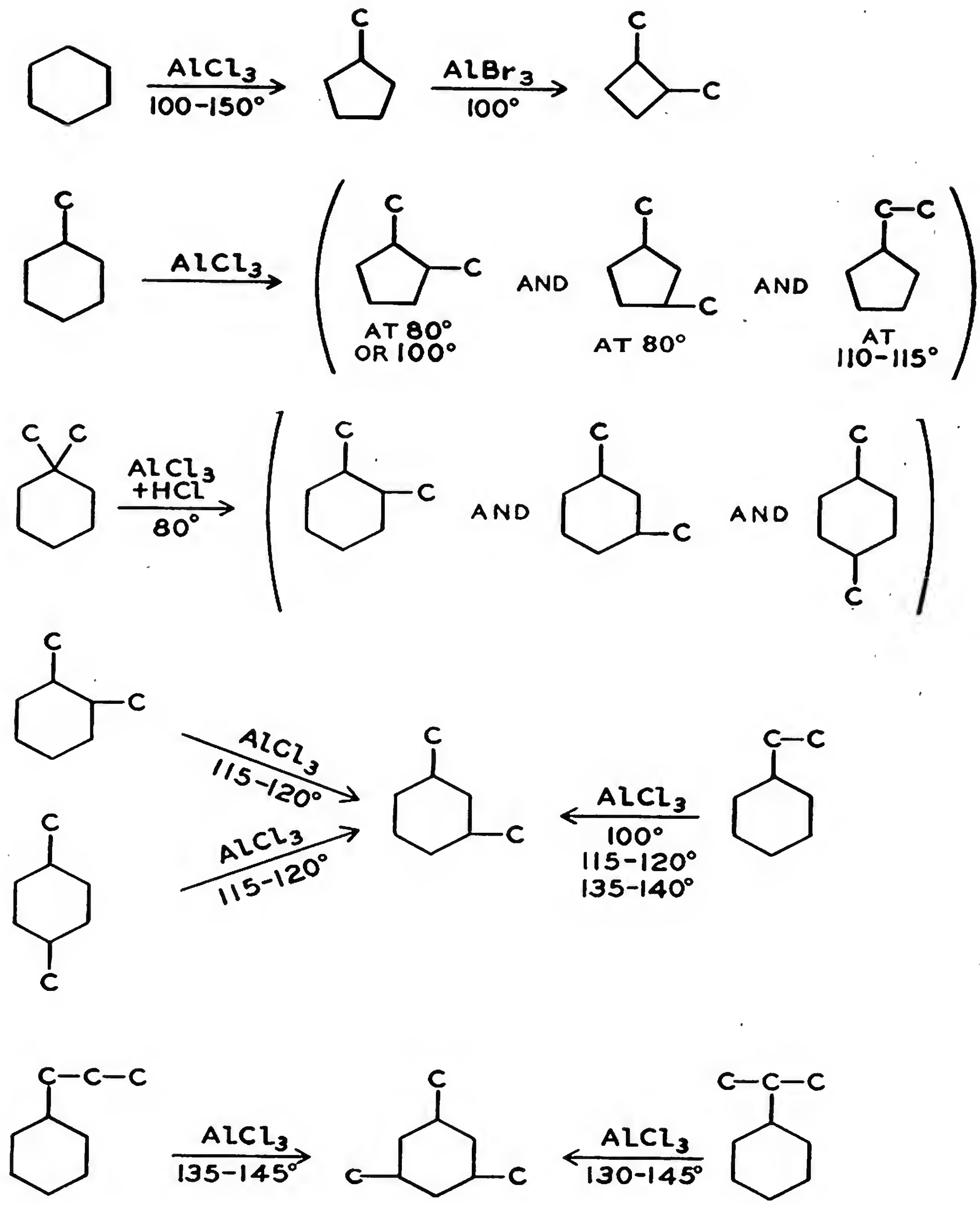
(3) Trimethylcyclohexane from *n*-propylcyclohexane treated for 7.5 hours at 135-145° with 30 per cent of aluminum chloride, or from isopropylcyclohexane treated for 7 hours at 130-145° with 23 per cent of the same catalyst.

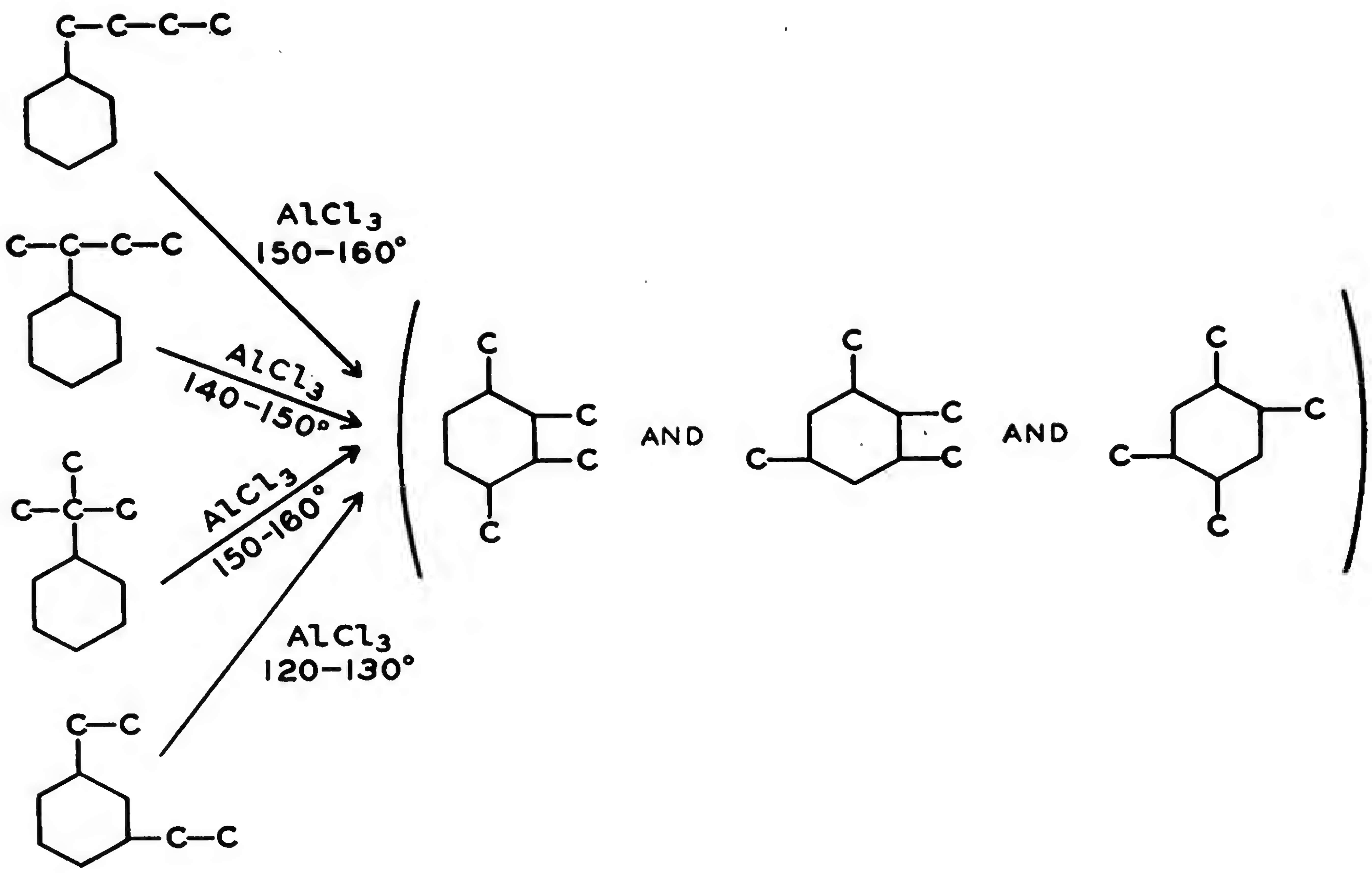
(4) Tetramethylcyclohexane from *n*-, *sec*-, or *tert*-butylcyclohexanes heated for 8 hours at 150-160° with aluminum chloride (20-23 per cent).

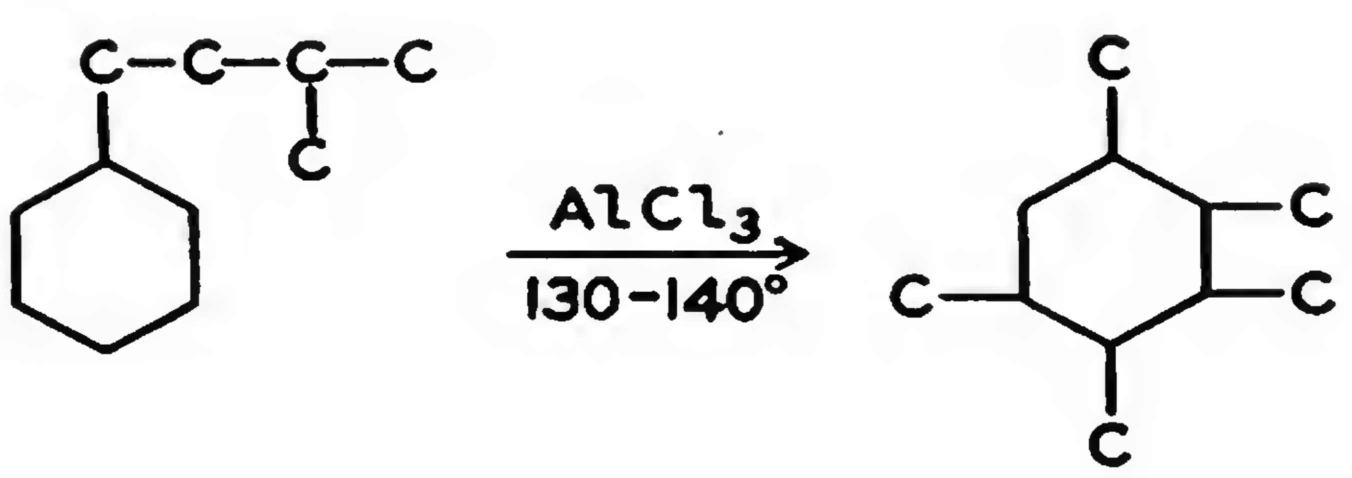
(5) Tetramethylcyclohexane from 1,3-diethylcyclohexane treated for 4 hours at 120-130° with aluminum chloride (23 per cent).

(6) Pentamethylcyclohexane, besides methylcyclohexane, tetramethylcyclohexane, *n*-butane and isobutane, from the treatment of isoamylcyclohexane for 5 hours at 130-140° with aluminum chloride (17 per cent).

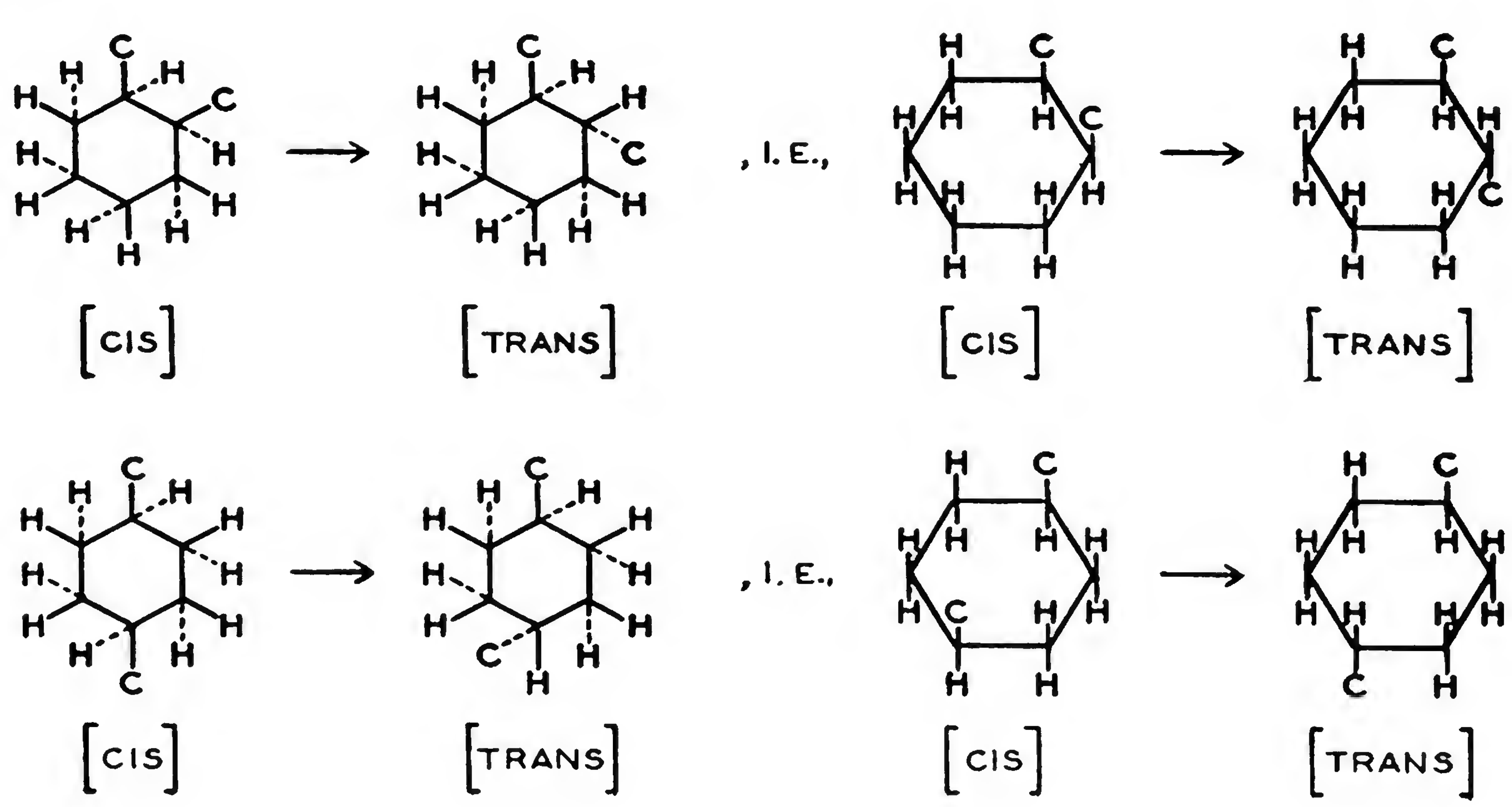
The formation of 1,3-dimethylcyclohexane was reported also from ethylcyclohexane and anhydrous aluminum chloride (10 per cent) at 135-140°.[599] 1,3,5-Trimethylcyclohexane resisted the action of aluminum chloride.[598ab] A 20 hours' treatment at 140-147° yielded 3 per cent of alkanes, 9 per cent of alkylcyclopentanes (trimethylcyclohexane isomers?), and 88 per cent of unchanged initial hydrocarbon. The isomerizations of cyclohexane and its homologs occurring in the presence of aluminum halides are summarized as follows:


ALCL3
100-150°
ALBr3
100°
ALCL3
AT 80° OR 100°
AND
AT 80°
AND
AT 110-115°
ALCL3
+HCL
80°
AND
AND
ALCL3
115-120°
ALCL3
115-120°
ALCL3
100°
115-120°
135-140°
ALCL3
135-145°
ALCL3
130-145°

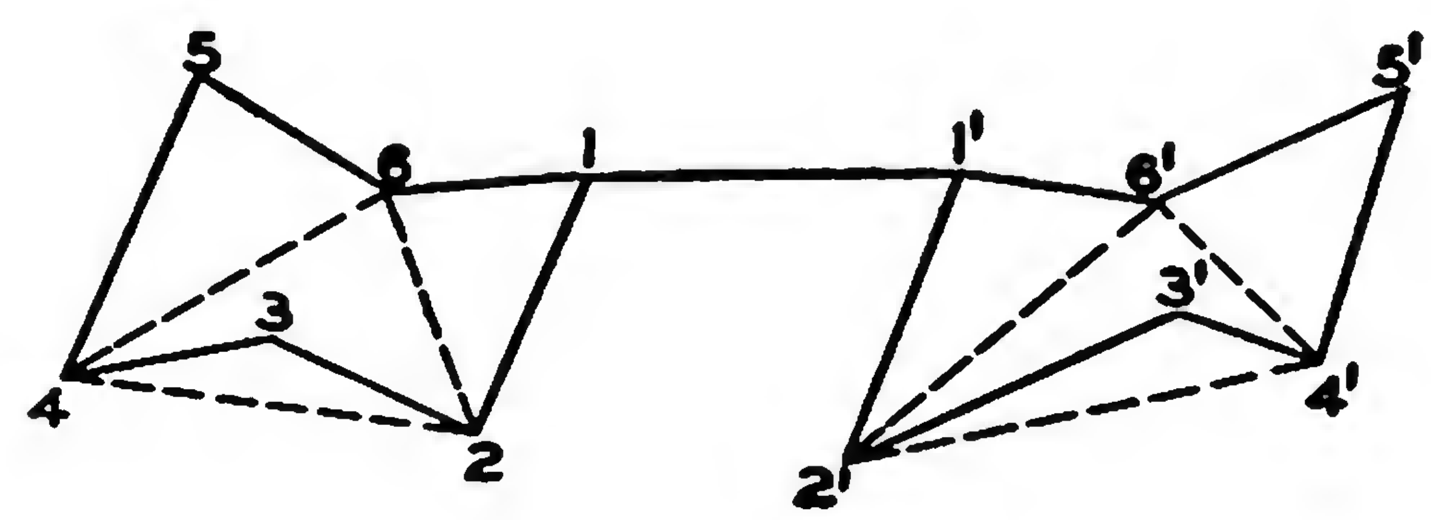




Passage of the *cis* forms of 1,2- and 1,4-dimethylcyclohexanes with hydrogen over nickel at 175° gave the *trans* forms.[671] The following diagrams are two of several equivalent ways of expressing these isomerizations:

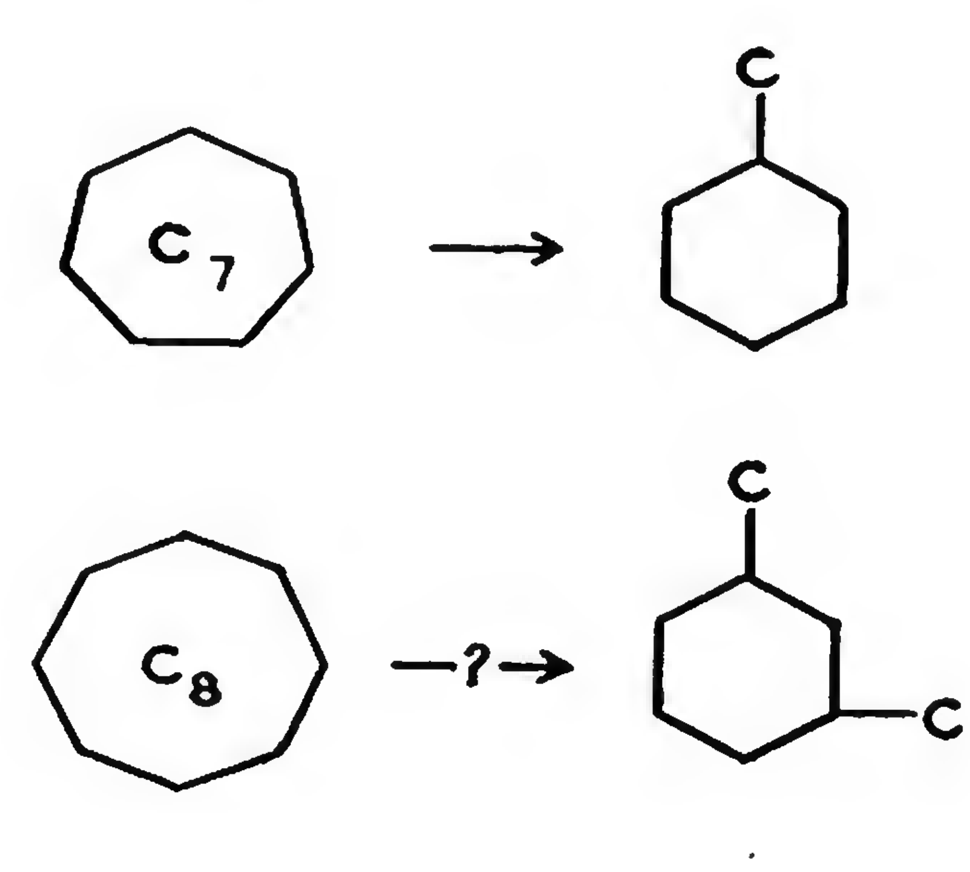


Dicyclohexyl (b.p. 234°/750 mm. Hg, $D_4^{20} = 0.8840$, $n_D^{20} = 1.4807$), treated for a long period with aluminum chloride at 15-20° or better at 100°, was converted into an isomer of lower boiling point, density, and index of refraction (b.p. 217-219°, $D_4^{20}=0.8592$, $n_D^{20}=1.4663$), which was taken as indicative of the presence of *trans-trans*-dicyclohexyl.[349] The product corresponds approximately to a previously described "labile" form of dicyclohexyl (b.p. 219.5-221.5°/750 mm. Hg, $D_4^{20} = 0.8809$, $n_\gamma^{20} = 1.47758$).[527] Low values of the physical constants of pure geometrical isomers are characteristic generally of stable structure and less free energy. *Trans* isomers, for example, have a higher vapor pressure at a given temperature.[681] Therefore, the lowered constants of the product may be indicative of two united ("chair") forms of cyclohexyl:

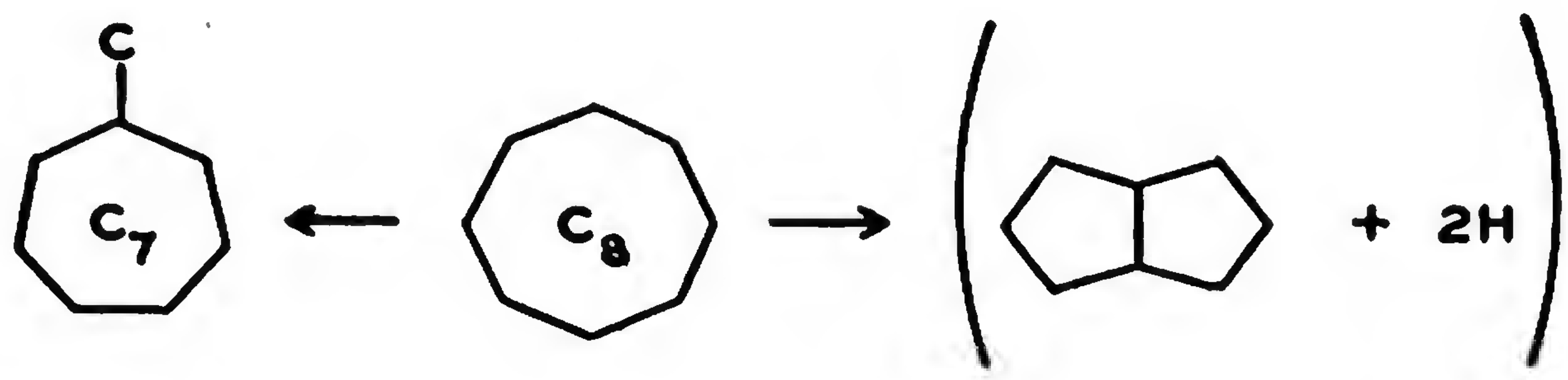


Other possibilities include the presence of methylcyclopentylcyclohexyl and/or dimethyldicyclopentyl.

Cycloheptane and Larger Cyclanes. Cycloheptane at 235° and cycloöctane at 205-210° isomerized to methylcyclohexane and dimethylcyclohexane, respectively, when passed as vapors over a nickel catalyst in the presence of hydrogen.[650] Higher temperatures caused a dehydrogenation to aromatics;[650] cycloheptane was converted partially into toluene by means of platinized charcoal and hydrogen at 300-340°.[594] Cycloheptane yielded 97-98 per cent of methylcyclohexane when treated with aluminum chloride at 117-125° for 20 hours.[598aa] The foregoing isomerizations are non-reversible reactions:



Platinum catalyzed the isomerization of cycloöctane into methylcycloheptane at 300°.[667] This product was accompanied by an equal amount of bicyclo[3.3.0]octane.



Cyclopentadecane and cycloheptadecane remained unchanged when heated with hydrogen iodide, indicating considerable ring stability.[485]

The isomerizations of cyclanes and cyclanes with saturated side-chains are given in Table 17, p. 290.

Conclusions

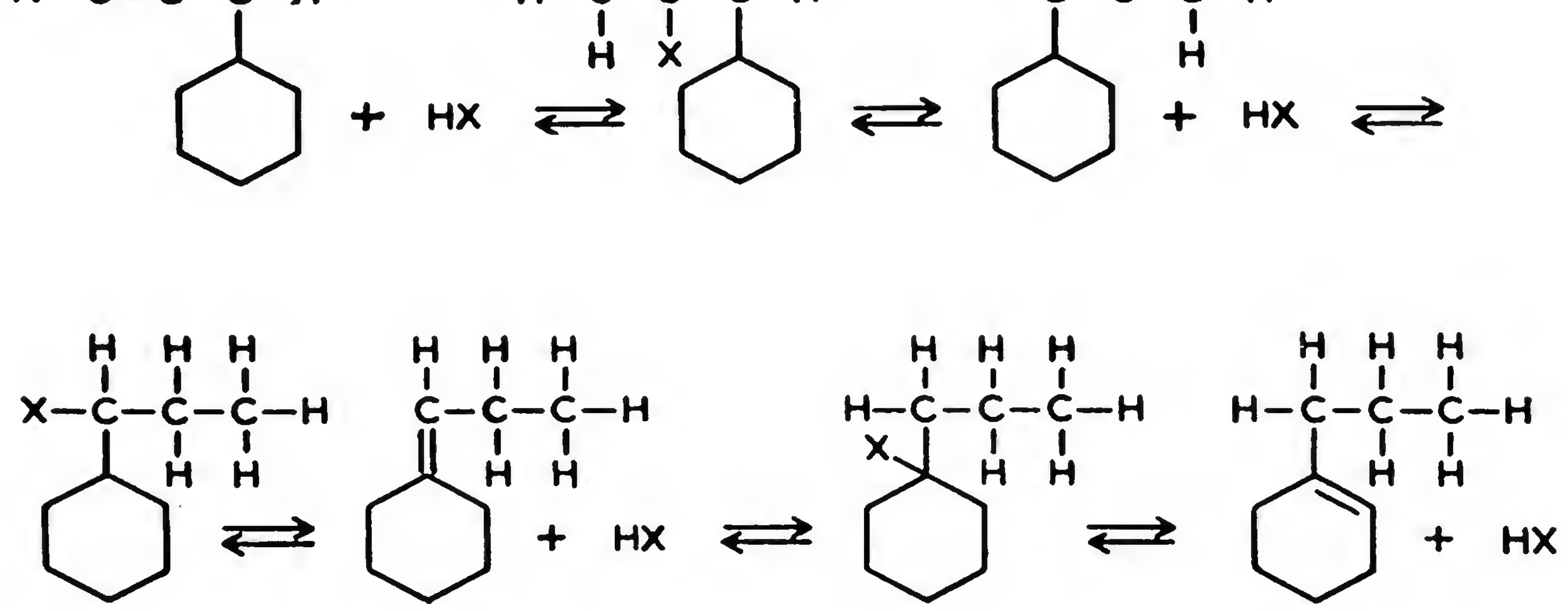
1. Cyclanes and their alkyl derivatives isomerize by changing into: alkenes, cyclanes of smaller ring size (with increased number of side-chains), cyclanes of same ring size (with altered side-chains or side-chains distributed about the ring as methyl groups), or cyclanes of increased ring size at the expense of a side-chain.

2. Cyclohexanes of unstable geometrical and multiplanar structures can be expected to isomerize into the corresponding stable form.

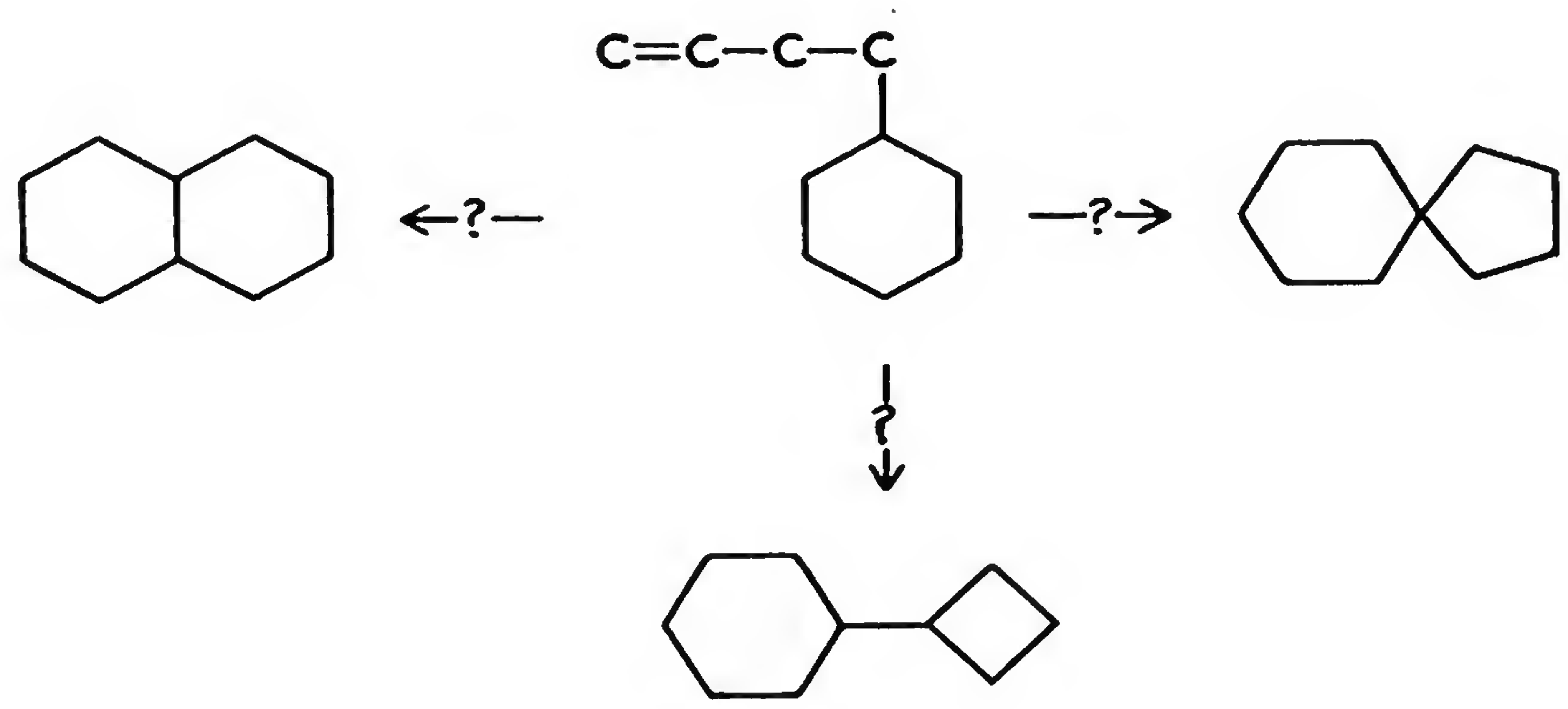
Cyclanes with Unsaturated Side-Chains

Mechanism

Cyclanes containing unsaturated side-chains are noted for their formation of cyclenes and alkadienes. The simplest isomerization observable consists of a change in the location of an unsaturated bond in the side-chain. The mechanism involved may be dehydrogenation plus cyclization, followed by decyclization plus hydrogenation. Addition-product formation and subsequent regeneration of the catalyst would account also for the reactions. With acid catalysts, in particular, a shift of the double bond into the ring may occur:



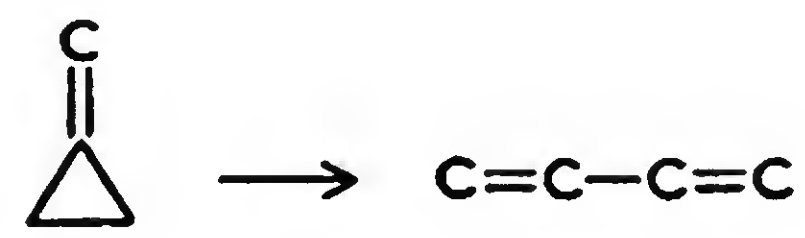
An isomerization of a cyclane with an unsaturated side-chain into a dicyclyl or into a bicyclane has not been reported to date. Isomerization should lead also to the spiranes, provided that the condition of strain does not decrease greatly the stability of the resulting isomer and, further, that the proper catalyst or reaction conditions can be found:



The reported isomerizations of cyclanes with an unsaturated side-chain into alkadienes can be considered as reactions resulting from ring instability (at temperature points where conjugated alkadienes are relatively stable).

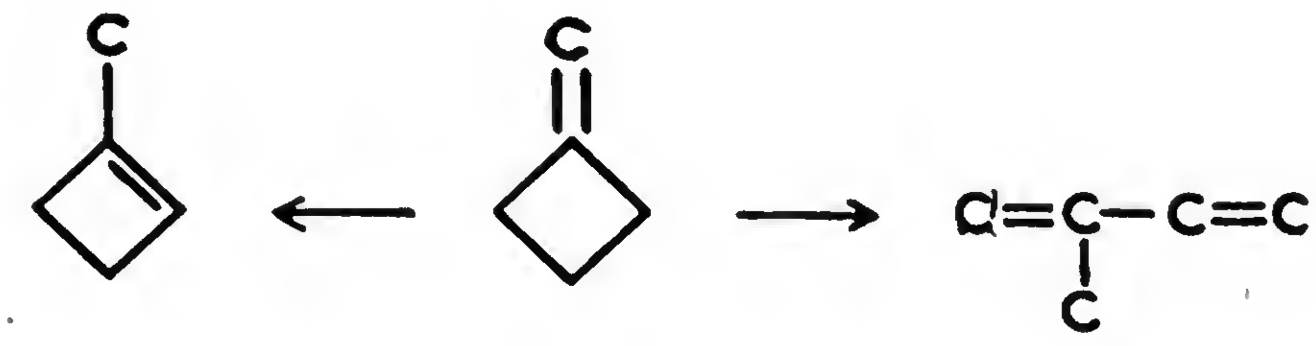
Isomerizations

Cyclopropanes. Methylenecyclopropane isomerized to butadiene-1,3 in the presence of alumina at 350°; [372]

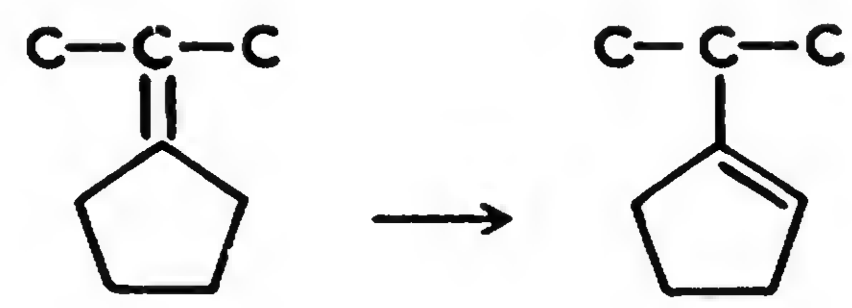


Vinylcyclopropane, although it has been prepared,[134] has not been studied from the standpoint of isomerization. Earlier preparations,[237, 289] taken to be vinylcyclopropane and upon which studies of isomerization were conducted, were shown by a later investigator [188] to consist essentially of methylenecyclobutane with some 1-methylcyclobutene-1. "Spirocyclane" [672] is the same mixture taken to be spiropentane.

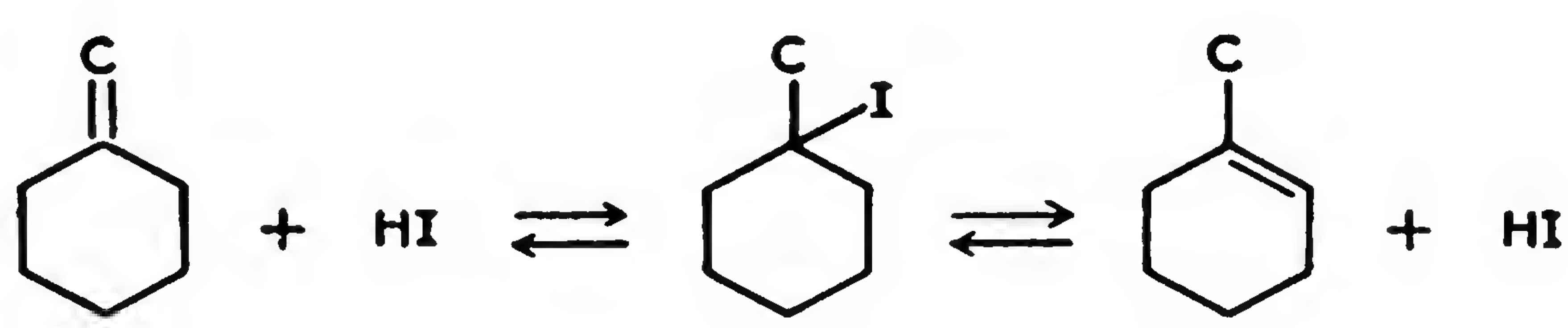
Cyclobutanes. Methylenecyclobutane isomerized to 1-methylcyclobutene-1 with alumina at 300°,[187, 189, 289] sodium at 180-185°,[672] or when heated with zinc bromide plus basic zinc bromide and dilute alcohol.[189] Alkalies, sulfuric acid, or traces of hydrogen bromide were effective also.[238] Formation of 2-methylbutadiene-1,3 (isoprene) and *p*-cymene occurred over alumina at the more elevated temperature of 395-430°.[140] Some pentene-2 is formed also; [140] this is indicative of a hydrogenation-scission of 1-methylcyclobutene-1.



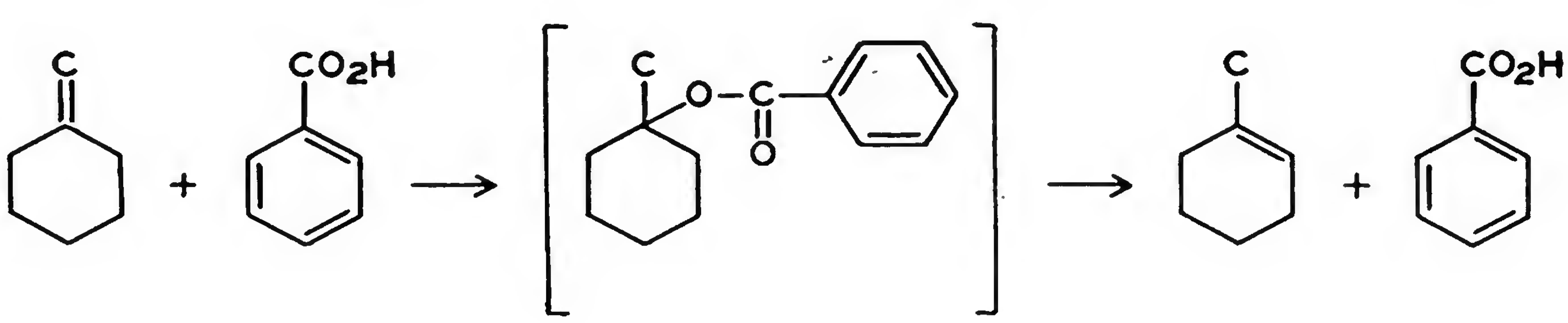
Cyclopentanes. Isopropylidenecyclopentane when heated 10 hours with alcoholic sulfuric acid gave 1-isopropylcyclopentene-1:[630]



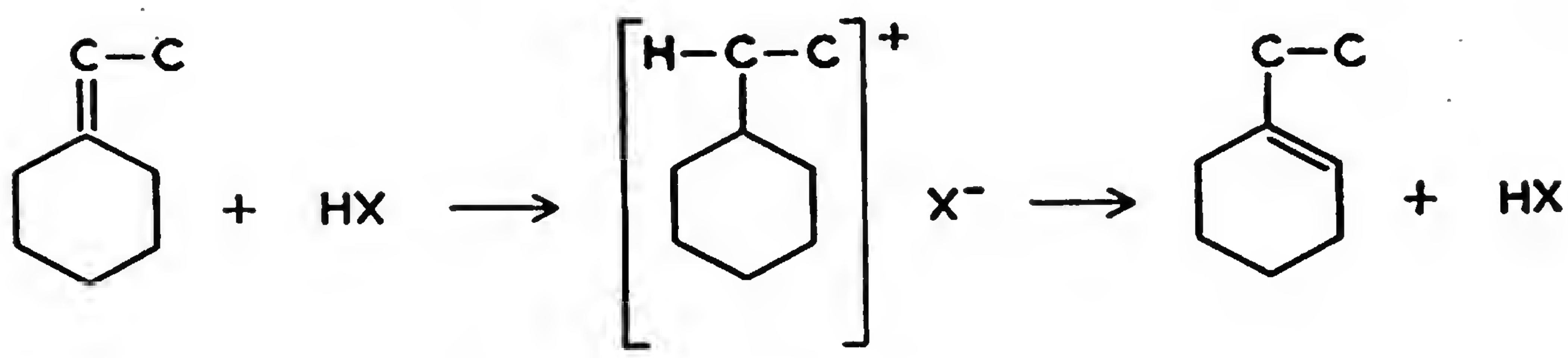
Cyclohexanes. Methylenecyclohexane isomerized partly to 1-methylcyclohexene-1 under the action of quinoline hydriodide plus quinoline, for 3 hours at 140°, or of benzoic acid for 7 hours at 170.[181] Quinoline alone is ineffective at the boiling point (145°) of the mixture, but quinoline hydriodide with an excess of quinoline is very effective when heated under reflux. The mechanism of isomerization was given as follows:



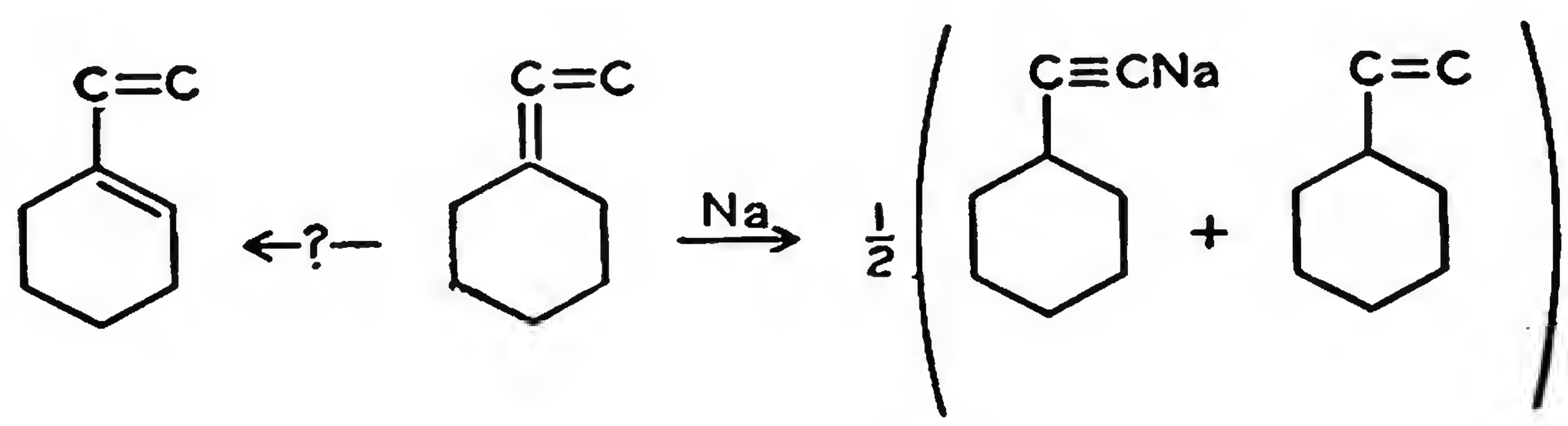
The requisite free hydrogen iodide was believed to result from thermal instability of quinoline hydriodide. The isomerization is reversible; alcoholic potash at 170° had no effect upon methylenecyclohexane.[181] Previous workers,[668] investigating the same reaction with quinoline hydriodide, considered it to be an isomerization of bicyclo[3.1.1]heptane ("1,3-methylenecyclohexane") into 1-methylcyclohexene-1. Methylenecyclohexane, when boiled with alcoholic sulfuric acid, also gives 1-methylcyclohexene-1.[623] The following mechanism describes the isomerization using benzoic acid (based upon the analogous hydrogen iodide example):



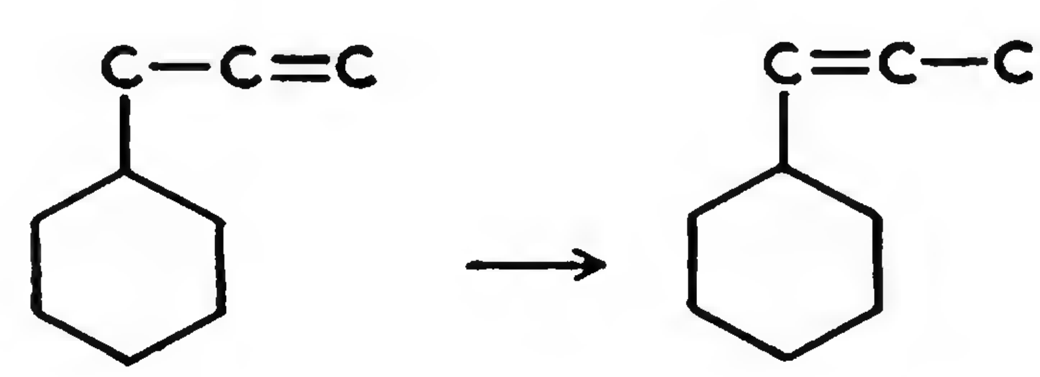
Ethylidenecyclohexane, heated for 6 hours with alcoholic sulfuric acid, formed 1-ethylcyclohexene-1.[629] This reaction is probably a general one in the presence of acids:



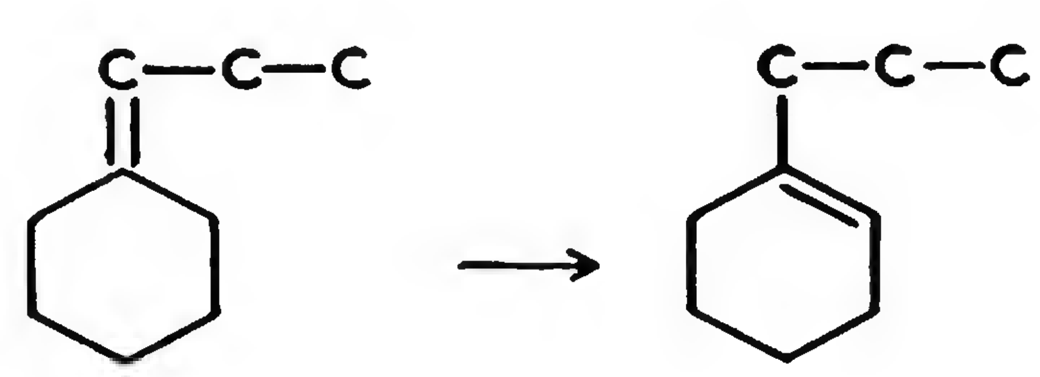
Vinylidenecyclohexane isomerized when heated to 170° with benzoic acid, probably into 1-vinylcyclohexene-1.[161] Sodium at 90-100° gave sodium cyclohexylacetylide, and cyclohexylethylene.[161] The formation of the last hydrocarbon is indicative of hydrogen disproportionation:



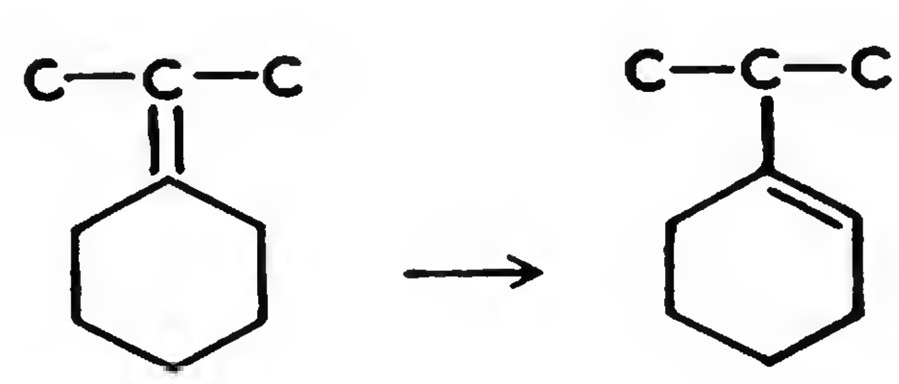
Allylcyclohexane at 500-650° gave numerous decomposition products, but probably also formed some propenylcyclohexane: [262]



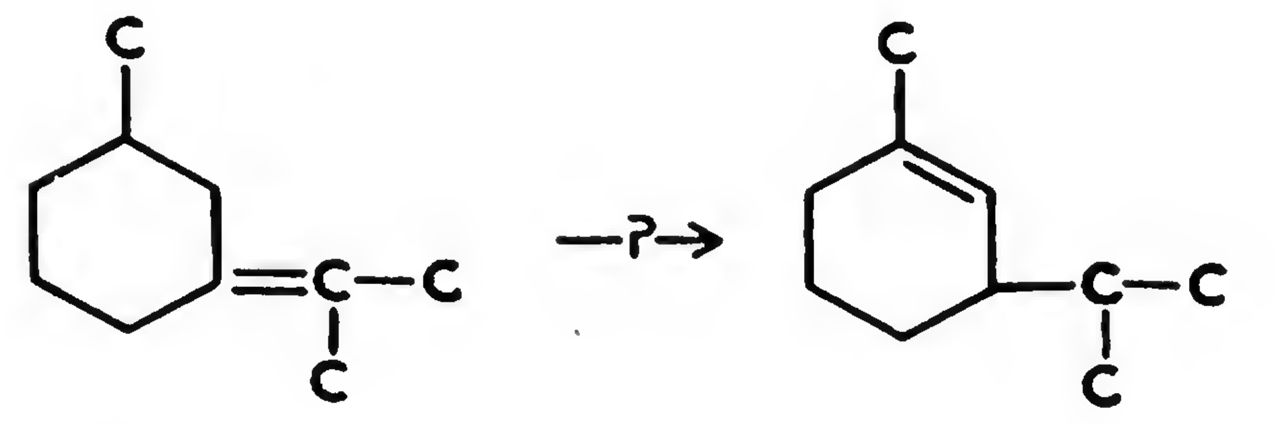
Propylidenecyclohexane, heated 10 hours with alcoholic sulfuric acid, yielded 90 per cent of 1-propylcyclohexene-1: [628]



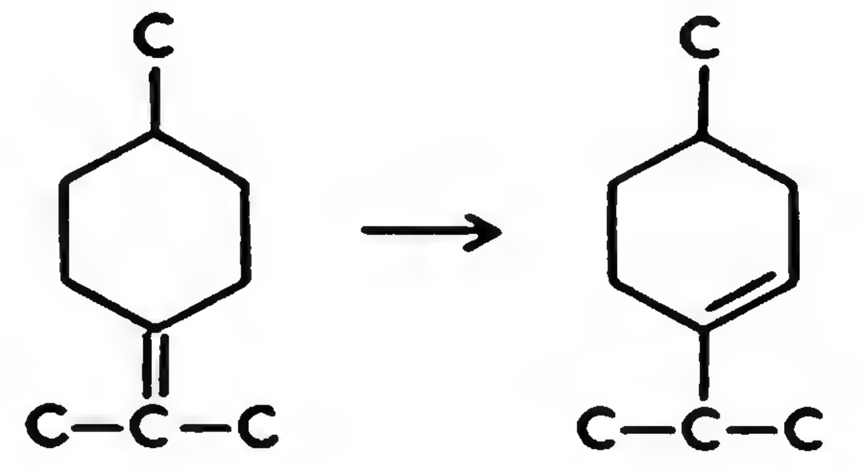
Isopropylidenecyclohexane, heated with alcoholic sulfuric acid, was converted partly into 1-isopropylcyclohexene-1: [631]



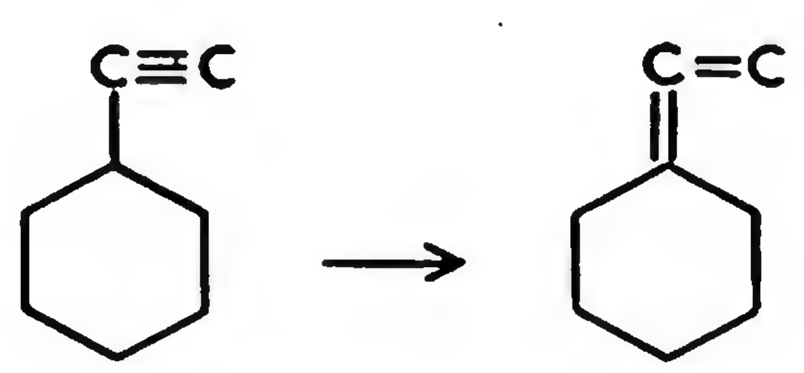
1-Methyl-3-isopropylidenecyclohexane, when heated 10 hours with alcoholic sulfuric acid, gave 20 per cent of an isomer thought to be 1-methyl-3-isopropylcyclohexene-1: [627]



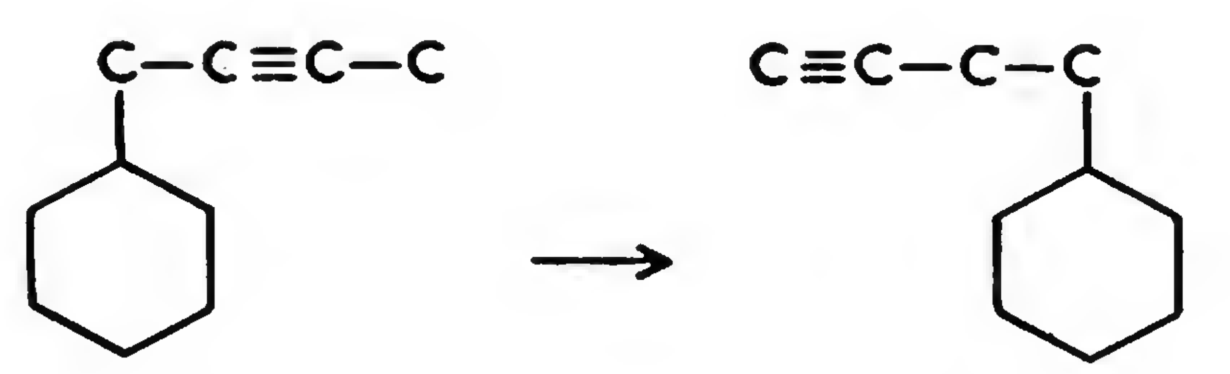
1-Methyl-4-isopropylidenecyclohexane (*i.e.*, $\Delta^{4(8)}$-menthene; dihydroterpinolene), heated under reflux for 1 hour with dilute sulfuric acid, gave 1-methyl-4-isopropylcyclohexene-3 (ordinary *dl*-menthene):[624, 626]



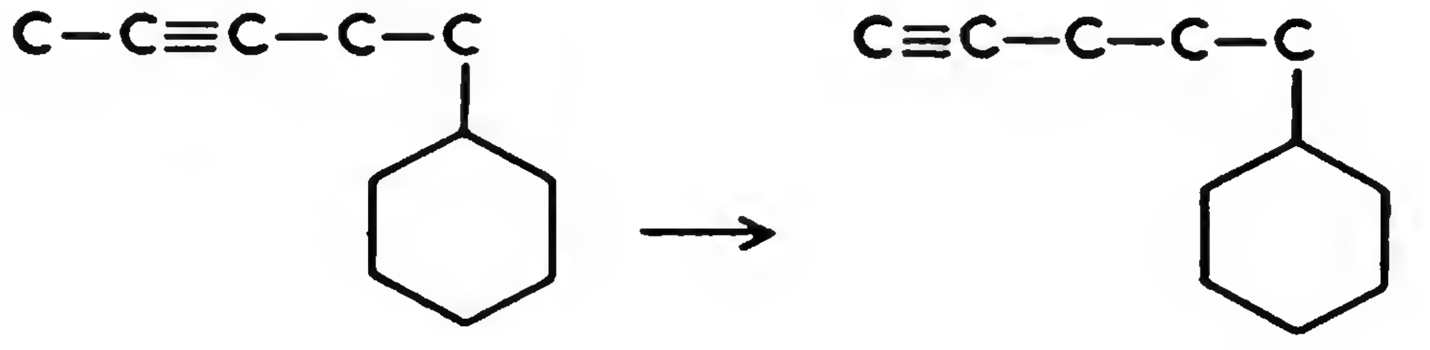
Cyclohexylacetylene isomerized to vinylidenecyclohexane (*i.e.*, cyclohexylideneëthylene) under the influence of alcoholic potash at 140°: [161]



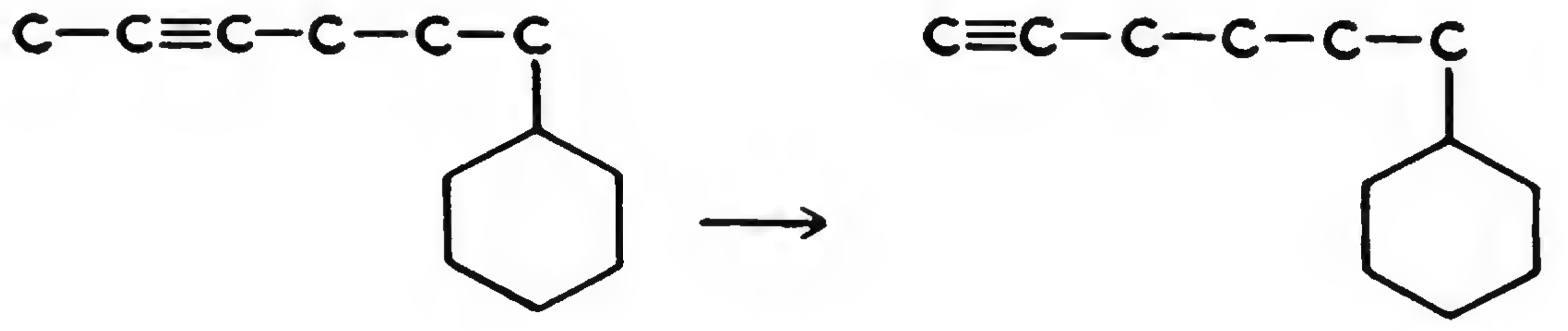
1-Cyclohexylbutyne-2, heated for 3 hours at 160° with sodamide and petroleum, gave 77 per cent of 4-cyclohexylbutyne-1.[81, 83] The petroleum served to dilute the reactants and to support the sodamide:



5-Cyclohexylpentyne-2, when heated at 160° for 2.5 hours with sodamide and petroleum, formed 76 per cent of 5-cyclohexylpentyne-1:[81]



6-Cyclohexylhexyne-2, when heated for 2 hours at 160° with sodamide and petroleum, produced 71 per cent of 6-cyclohexylhexyne-1: [81]



Isomerizations of cyclanes with unsaturated side-chains are given in Table 18, p. 304.

Conclusions

1. Cyclanes with unsaturated side-chains isomerize by changing into alkadienes, cyclenes, or cyclanes having an altered location of unsaturation in the side-chain.

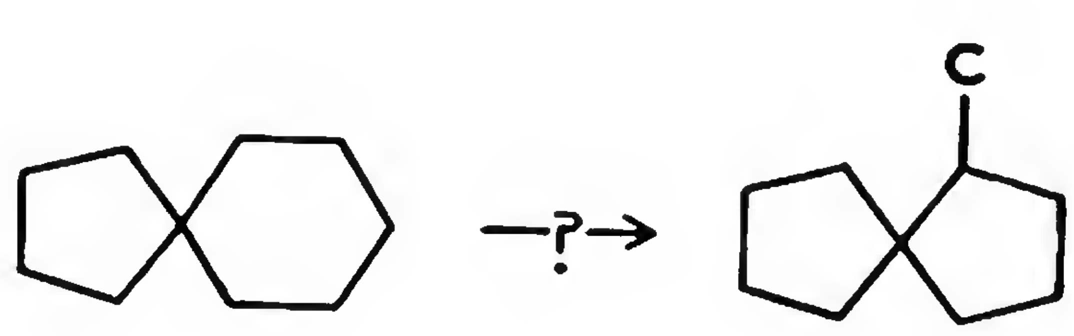
2. The isomerizations exhibited by unsaturated side-chains are subject to the rules of the corresponding unsaturated aliphatic hydrocarbons.

3. Numerous cycloalkylidenes become alkyl cyclenes when treated with acids.

Spiranes

Isomerizations

The spiranes are a group of hydrocarbons that has been neglected from the isomerization standpoint. Spiro[4.5]decane, however, has been isomerized by slow passage over platinized charcoal at 190°.[671c] The physical constants of the isomer product (b.p. 185.5-186°/750 mm. Hg, $D_4^{20} = 0.8730$, $n_D^{20} = 1.4683$) correspond to those of *trans*-decalin (b.p. 185-186.5°, $D_4^{21.5} = 0.8682$, $n_D^{21.5} = 1.4675$), but the product's stability toward dehydrogenation by platinized charcoal at 300° [673] is against this assumption. The isomer may be 1-methylspiro[4.4]nonane:



Further data on isomerization of spiranes are given in Table 19, p. 306.

Bicyclanes and Bicyclanes with Saturated Side-Chains

Mechanism

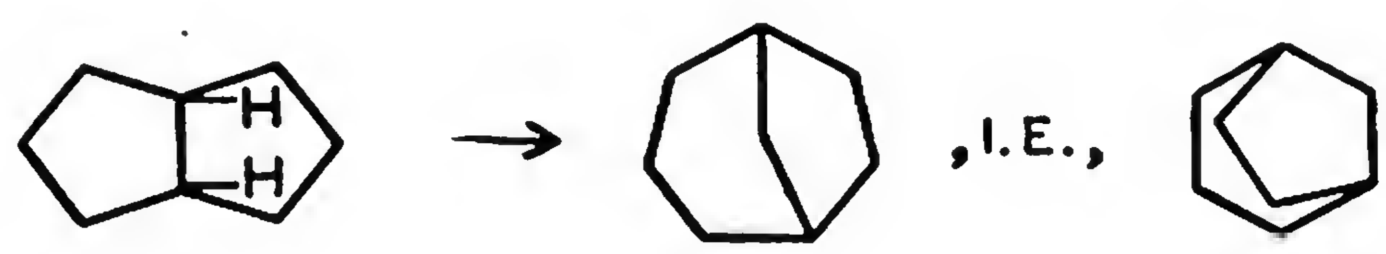
Bicyclanes (bicycloparaffins) and saturated homologs, although extensively encountered in the literature, have been studied only slightly with regard to isomerization. Mechanisms encountered in the previous sections can be applied, but these will require special consideration of the bicyclic structure. Thus, conditions of strain in the molecule to be isomerized may effect geometrical isomerization and changes in ring size. Derivatives of bicyclo[3.1.1]heptane, *i.e.*, of norpinane, exist theoretically in multiplanar strainless forms.[205]

Isomerizations

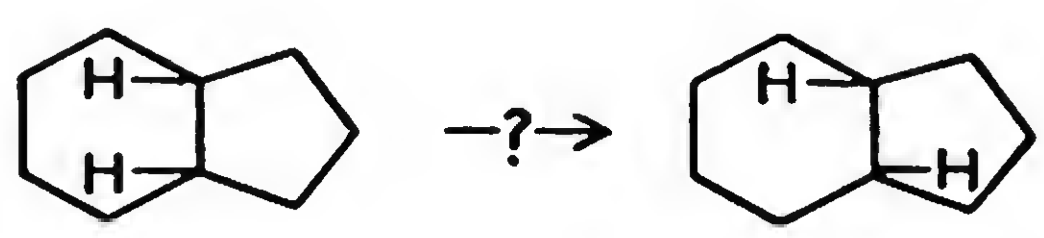
Bicycloheptanes. The isomerization of 2,2,3-trimethylbicyclo[2.2.1]-heptane (*i.e.*, dihydrocamphene or isocamphane) by iodine and hydriodic

acid at 240-295° has been reported.[354] Starting material and the principal fraction of the product were both mixtures obviously containing impurities; the facts warrant a reëxamination of the reaction.

Bicycloöctanes. Cyclopentane rings in a condensed ring system can be isomerized to cyclohexane rings by the action of aluminum chloride. *Cis*-bicyclo[3.3.0]octane isomerized partly into bicyclo[3.2.1]octane when treated from 2 to 48 hours with aluminum chloride (28.6 per cent) at room temperature.[37] This reaction involves, in its over-all aspect, the ruptures of one C—H bond and one C—C bond and a recombination in new directions:



Bicyclononanes. The isomerization of *cis*-bicyclo[4.3.0]nonane (*i.e.*, *cis*-hydrindane), probably into the *trans* form, occurred in 12 hours of treatment at 100° with dry aluminum bromide (43 per cent).[674] This reaction formed also: an unidentified C_9H_{16} isomer, a crystalline compound $C_{27}H_{42}$ (m.p. 192-193°), and an aluminum bromide plus hydrocarbon complex.

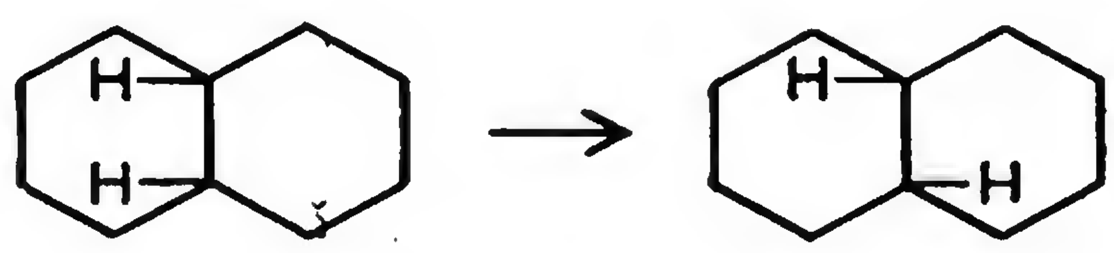


[CIS] [TRANS]

Methylhydrindane isomerized to dimethylbicycloöctane in the presence of molybdenum sulfide.[293]

Bicyclodecanes. *Cis*-bicyclo[4.4.0] decane (*i.e., cis*-decalin), treated for 12 hours at 100° with aluminum bromide (25 mole per cent) in the absence of moisture, gave an upper layer containing the *trans* form (about 6 per cent of the theoretical yield) and some isomeric $C_{10}H_{18}$ (about 4 per cent of the theoretical yield, b.p. 170-175°).[673] *Cis*-bicyclo-[4.4.0]decane containing dissolved aluminum bromide (31.25 per cent), when subjected to a slow stream of hydrogen bromide, gave an upper layer containing the *trans* form and a lower one of the composition $C_{10}H_{18}(AlBr_3)_2$.[674] Further studies [676] showed that *cis*-bicyclo[4.4.0]-decane, when treated with a technical grade of aluminum chloride at room temperature for 22 hours, gives an 85 per cent yield of the *trans* isomer (b.p. 184.0-186.5°). Heating of the reaction mixture increased the amount of lower-boiling products, as in a reaction of the *cis* form with aluminum chloride (3 moles:1 mole) at 100° for 12 hours. Treatment of the *cis* form for 14 hours at 100° in the presence of a technical grade of aluminum chloride, containing 3 per cent of iron chloride, gave

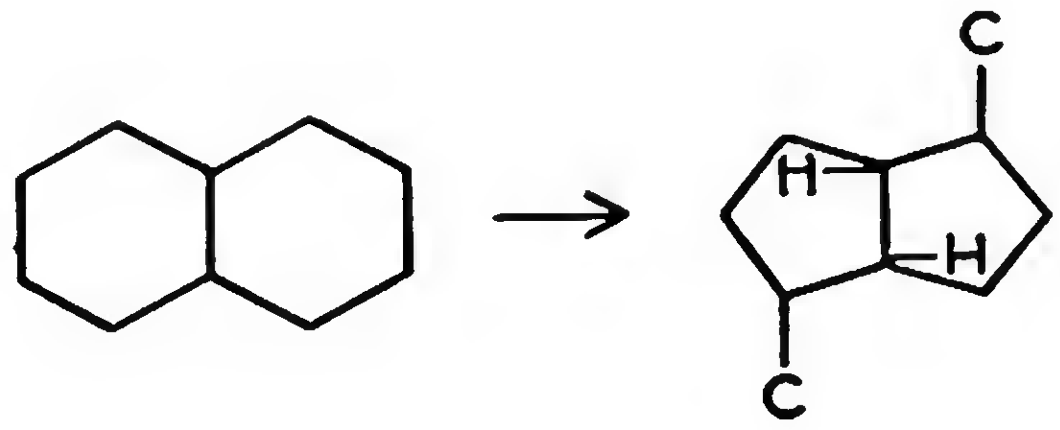
42.2 per cent of the *trans* isomer (b.p. 184.0-186.5°) and 50 per cent of lower-boiling products. Still later studies[677] with *cis*-decalin and aluminum chloride at 175-210° gave indications (index of refraction measurements) of *trans*-decalin and a dimethylbicyclo[3.3.0]octane as products. A nickel-cobalt-aluminum alloy has been used to isomerize *cis*-decalin into the *trans* form at 300° under 50 atmospheres' initial pressure of hydrogen.[545a] *Cis*-decalin, heated with molybdenum trisulfide under hydrogen pressure, gave 40 per cent of *trans*-decalin and 8 per cent of dimethylbicyclo[3.3.0]octane at 425-430°, whereas 52 per cent of the *trans* form resulted at 360-370°:[449]



[CIS] [TRANS]

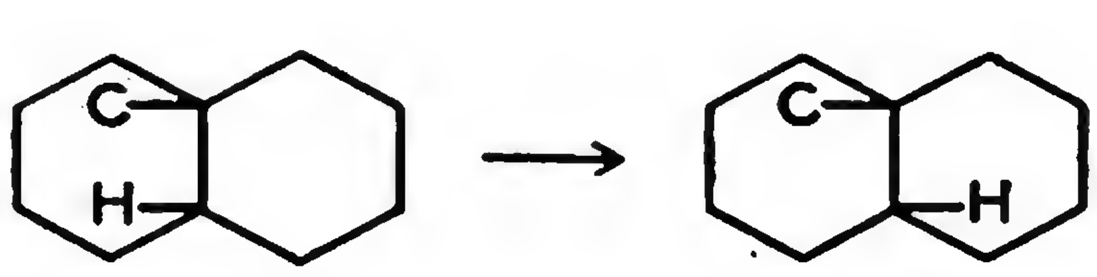
The heats of combustion of liquid *cis*-decalin and liquid *trans*-decalin at 25° and one atmosphere constant pressure are 1502.4 ± 0.1 and 1500.3 ± 0.1 kilocalories per gram-mole, respectively.[131b] Subtraction of the second heat quantity from that of the first gives 2.1 ± 0.14 kilocalories per gram-mole as the exothermic heat of isomerization of *cis*-decalin into the *trans* form.

Trans-bicyclo[4.4.0]decane (*i.e.*, *trans*-decalin), when heated with catalysts, undergoes a more severe isomerization, according to later workers. Commercial decalin (75 per cent *trans* form) under the action of aluminum chloride (24.2 per cent) for 24 hours at 130° isomerized partly into *trans*-2,6-dimethylbicyclo[3.3.0]octane (2-5 per cent), and at the same time produced small amounts of monocyclic hydrocarbons.[291] From 50-70 per cent of decalins were recovered (mainly *trans* form).

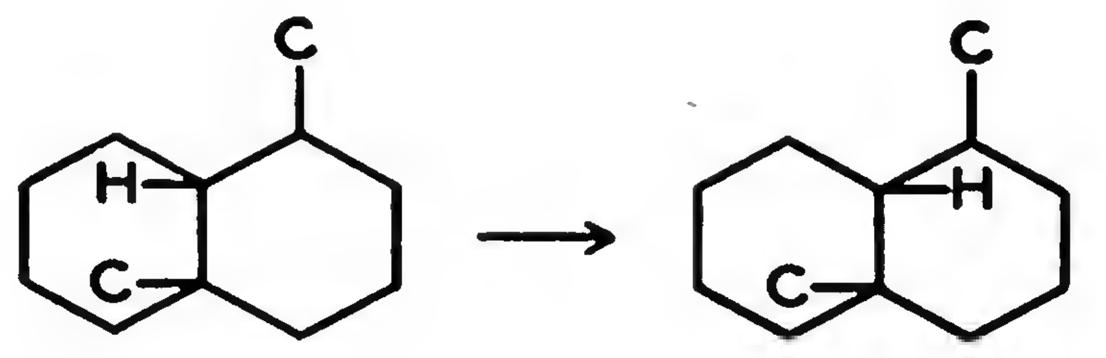


Molybdenum sulfide catalyzed the isomerization of *trans*-decalin into dimethylbicyclooctane at high temperatures.[293]

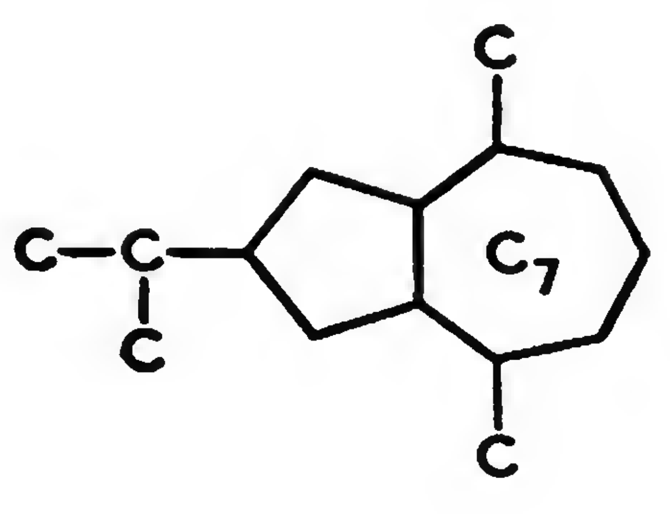
Cis-1-methylbicyclo[4.4.0]decane (*i.e.*, *cis*-9-methyldecalin) formed the *trans* isomer when treated with aluminum chloride at 20°:[252]



1,10(or 4,9)-Dimethyldecalin (mainly *cis*), treated with an equal weight of aluminum chloride for 2 days, gave the *trans* form:[351]



2,6 - Dimethyl - 9 - isopropylbicyclo[5.3.0]decane (*i.e.*, β - vetivane) yielded a less strained form upon 3 days' contact with aluminum chloride.[395b] This product was distinctly different from α-vetivane, which is still another stereoisomer.



[Isomerizes]

The experimental data on isomerization of bicyclanes and bicyclanes with saturated side-chains are given in Table 20, p. 308.

Conclusions

1. Two types of isomerization have been observed in the group of saturated bicyclanes, namely, (a) conversion of *cis* into *trans* forms by rotations at the junction of the 2 rings, and (b) changes in ring size.

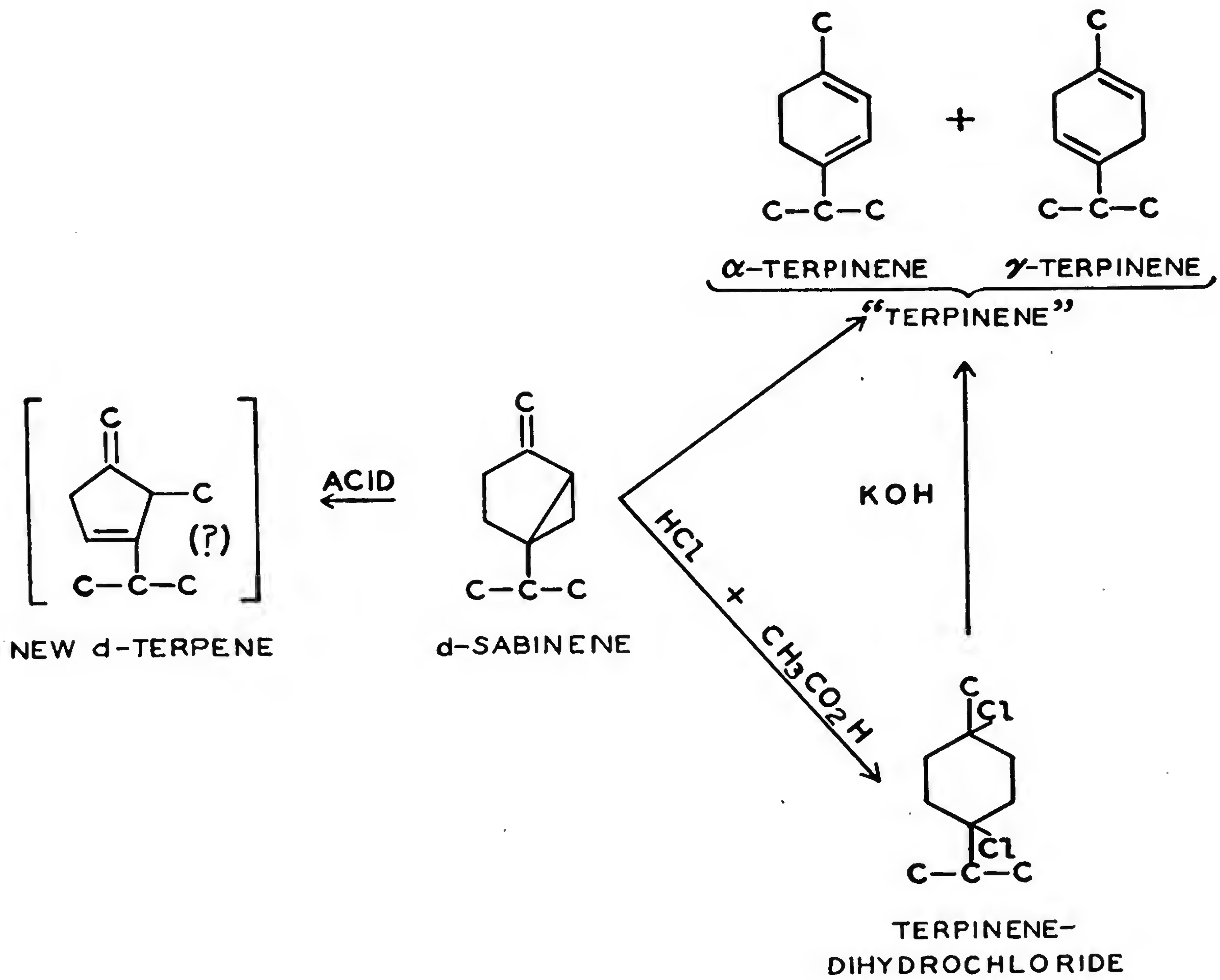
2. Cyclohexane rings within bicyclic hydrocarbons can change into cyclopentane rings, and *vice versa*.

Bicyclanes with Unsaturated Side-Chains

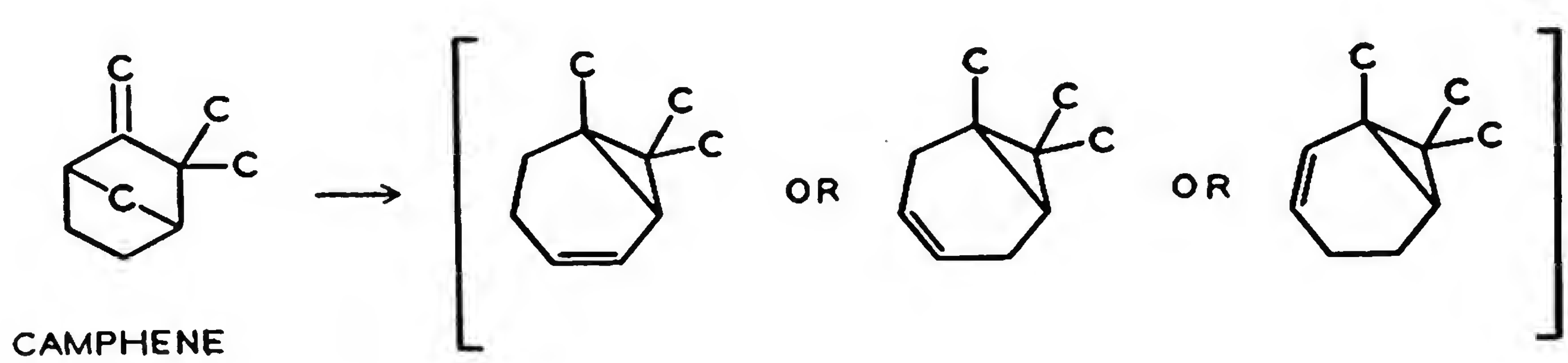
Isomerizations

Bicyclohexanes. *d* - 1 - Isopropyl - 4 - methylenebicyclo[3.1.0]hexane (*i.e.*, *d*-sabinene), heated under reflux with dilute sulfuric acid, formed much α- and γ-terpinenes.[622] *d*-Sabinene, heated with either aqueous or alcoholic sulfuric acid, formed also a dextrorotatory five-carbon-ring terpene, probably *d*-1-isopropyl-4-methylene-5-methylcyclopentene-1 (*i.e.*, *d*-1-methylene-2-methyl-3-isopropylcyclopentene-3).[533] The same five-carbon-ring isomer was formed when *d*-sabinene was treated with formic acid at $-20°$, or with acetic acid plus 50-per cent sulfuric acid at room temperature.[533] Formic acid, and acetic acid plus sulfuric acid, as catalysts,[533] gave also the *d*-monoformate and the monoacetate of terpineol-4, respectively.[534] Sabinene can be converted also into "terpinene" by a

"delayed isomerization" involving formation of terpinene-dihydrochloride and its subsequent dehydrohalogenation.[621, 622]



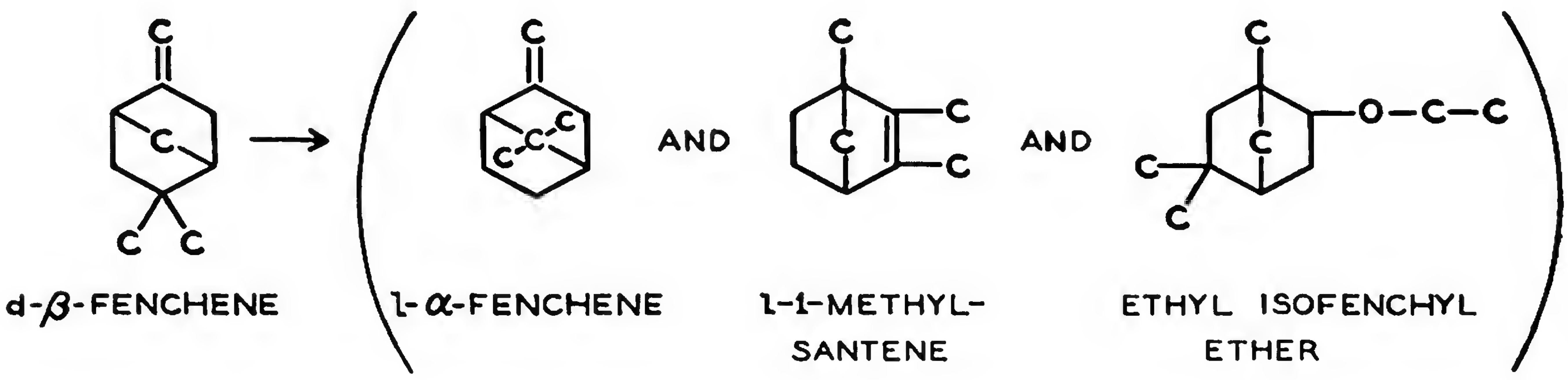
Bicycloheptanes. 2,2 - Dimethyl - 3 - methylenebicyclo[2.2.1]heptane (*i.e.*, camphene) was passed unchanged through a "Suprax" glass tube at 360-370°, which is indicative of its stability.[12] However, camphene when treated with phosphoric acid at 200°, formed an isomer and a diterpene.[201] Three structures were proposed tentatively for the isomer:



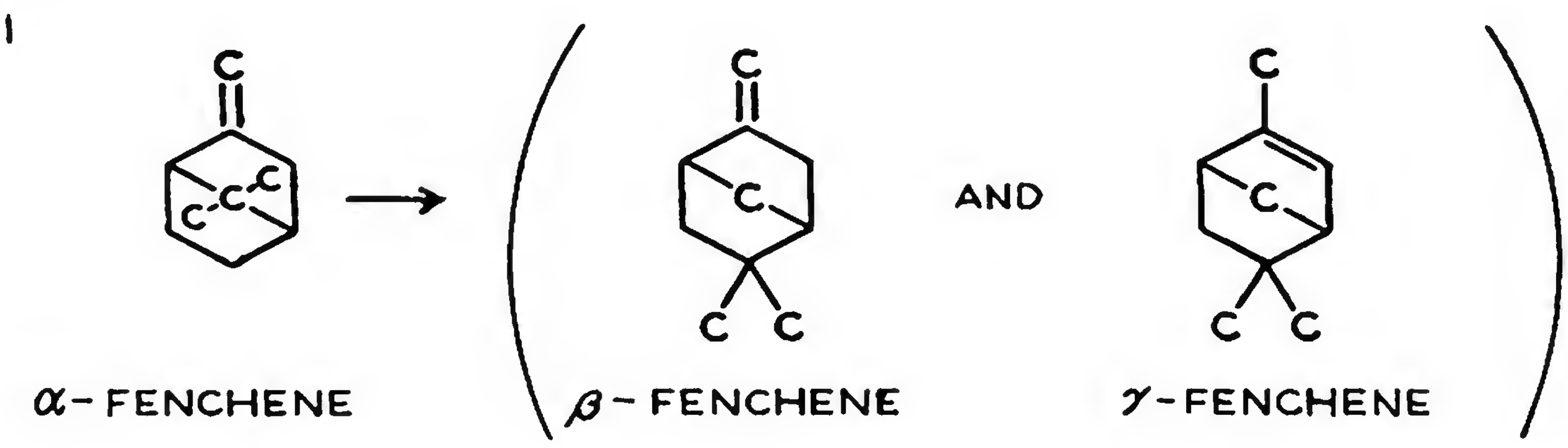
The proposed structures are probably incorrect, since the fused cyclopropane rings (if temporarily formed) would be attacked severely at 200° by the phosphoric acid.

d-2,2-Dimethyl-5-methylenebicyclo[2.2.1]heptane (*i.e.*, *d*-β-fenchene or *d*-2,2-dimethyl-5-methylenenorcamphane), heated under reflux with ethanol containing a small amount of dilute sulfuric acid or some potas-

sium hydrogen sulfate, underwent isomerizations to *l*-2-methylene-7,7-dimethylbicyclo[2.2.1]heptane (*i.e.*, *l*-α-fenchene or *l*-2-methylene-7,7-dimethylnorcamphane) and *l*-1,2,3-trimethylbicyclo[2.2.1]heptene-2 (*i.e.*, *l*-1-methylsantene or *l*-1,2,3-trimethylnorcamphene-2).[320a] Ethyl isofenchyl ether was formed in considerable amounts as a by-product. These isomerizations involve Wagner-rearrangements:*



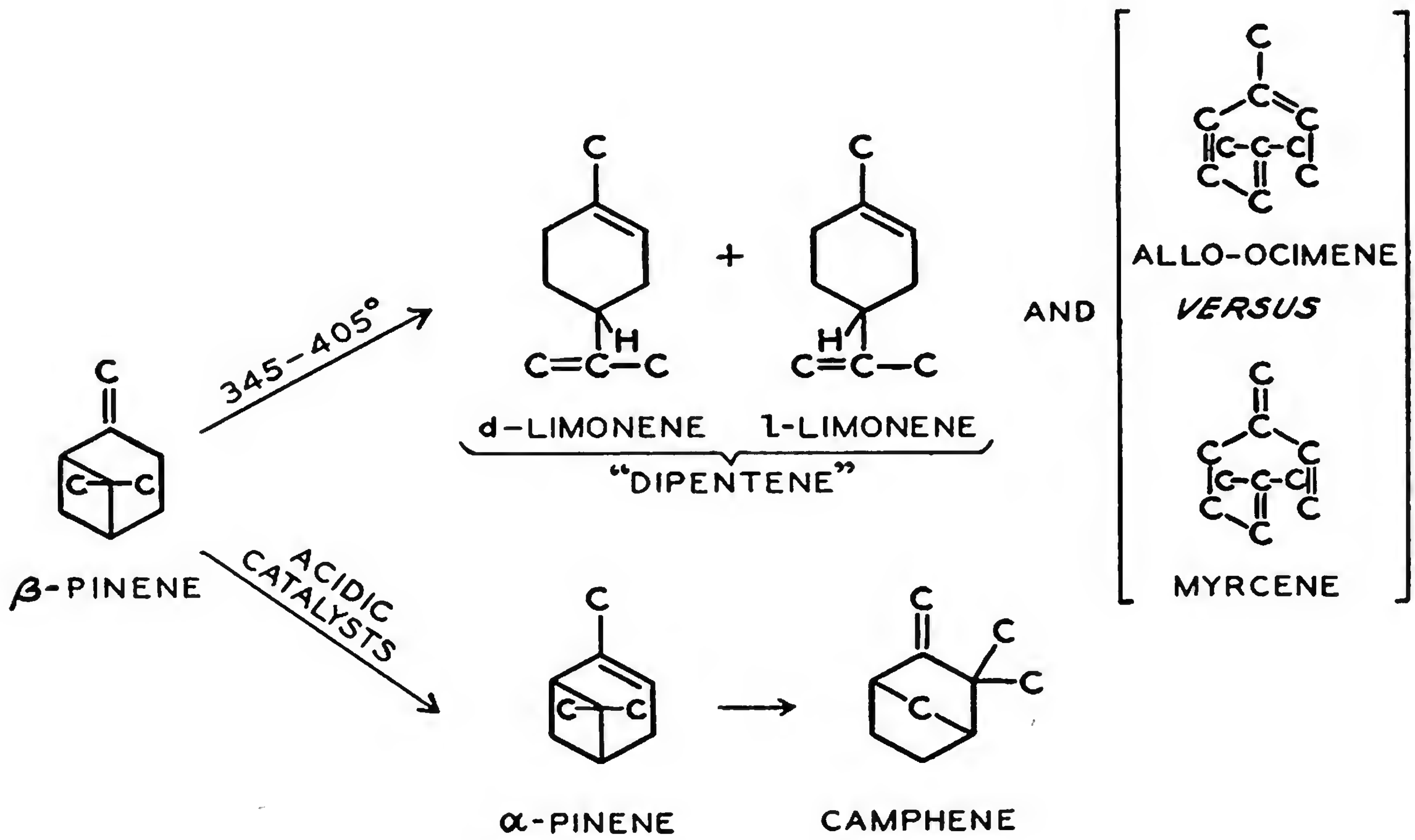
dl-2Methylene-7,7-dimethylbicyclo[2.2.1]heptane (*i.e.*, *dl*-α-fenchene) was completely isomerized to a mixture of 2,2-dimethyl-5-methylene-bicyclo[2.2.1]heptane (*i.e.*, β-fenchene) and 2,5,5-trimethylbicyclo[2.2.1]-heptene-2 (*i.e.*, γ-fenchene or 2,5,5-trimethylnorcamphene-2) by a 7-15 minutes' treatment with potassium hydrogen sulfate at the boiling point of the mixture:[320a]



2-Methylene-6,6-dimethylbicyclo[3.1.1]heptane (*i.e.*, β-pinene or nopinene) when passed through a "Suprax" tube at 345-350° gave allo-ocimene (25 per cent) dipentene, and some unconsumed β-pinene.[12] This reaction is related closely to the isomerization of α-pinene into allo-ocimene (considered later). Recent work [217b] indicates that *l*-β pinene is converted at 400-405° into *l*-limonene, myrcene, α-camphorene, and other polymers of myrcene. No evidence was obtained for an isomerization to allo-ocimene. Numerous acidic catalysts are known which convert β-pinene successively into α-pinene and then into camphene.[459a, 502, 503, 504,]

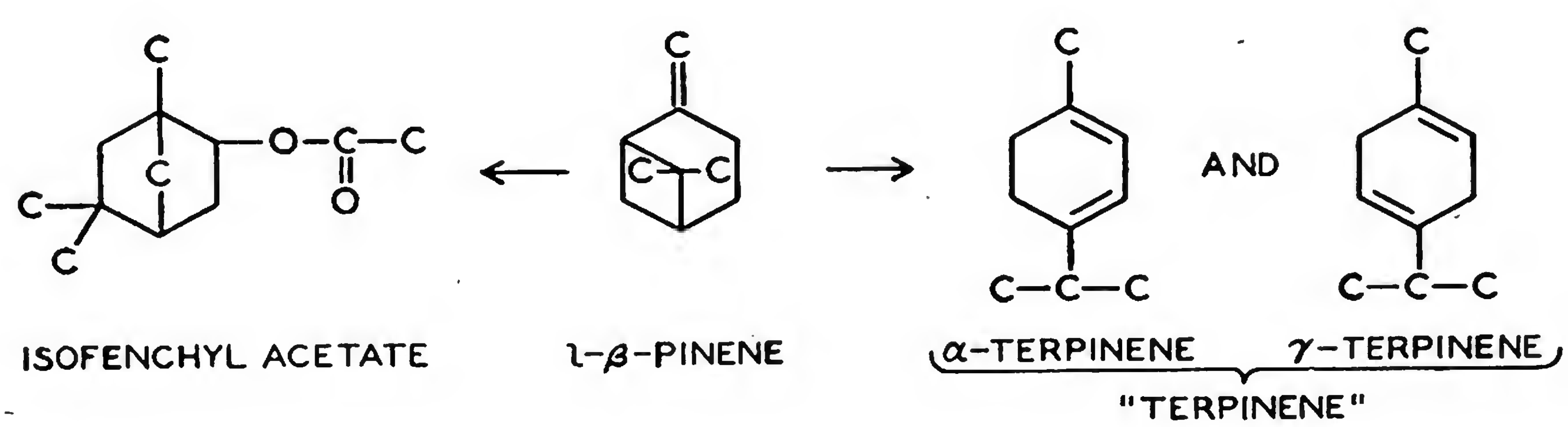
* The following structural formulas for α-, β-, and γ-fenchenes, 1-methylsantene, and ethyl isofenchyl ether are oriented so that the 2 uppermost carbon atoms are immobile, which enables a comparison to be made with the structure of cyclofenchene (*supra*). The last hydrocarbon may be considered as a probable intermediate for the given examples of isomerization, but its present non-isolation seems to indicate the operation of a mobile system of diyl forms, such as 1,3,3-trimethyl-tricyclo-[2.2.1.0^{2,6}]hepta-2,6-diyl, rather than a closed, true tricyclic structure.

504a, 508, 508a, 509, 510, 511, 511a, 512a, 513, 514. α-Pinene is considered to be a less strained molecule than β-pinene.[204]



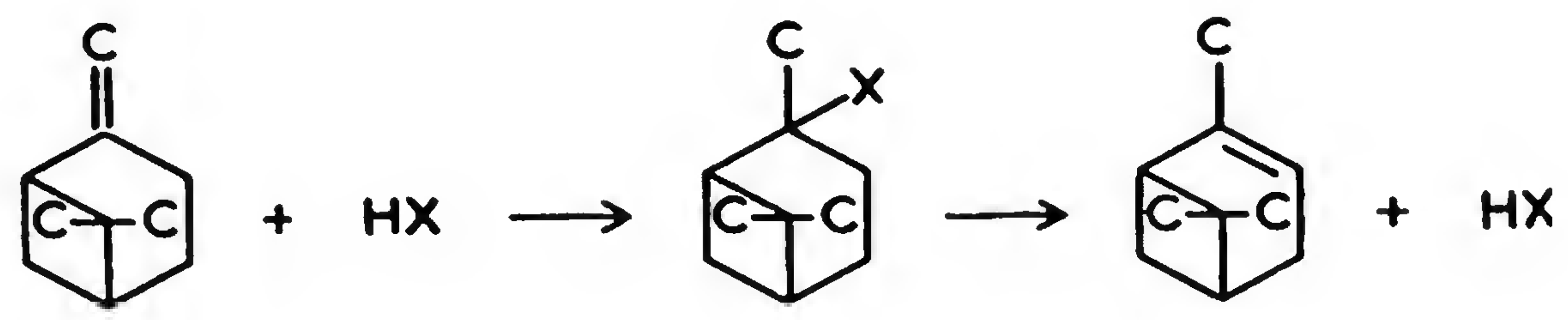
l-β-Pinene, treated with palladium black and hydrogen at room temperature, undergoes isomerization by double-bond shift, forming *l*-α-pinene.[466] This reaction is irreversible, since similarly treated *l*-α-pinene does not undergo isomerization.[466, 663]

β-Pinene, heated under reflux for 1.5 hours with fuller's earth, gave "terpinene" and a polymer called "dipinene."[610] *l*-β-Pinene, when heated for one hour at 60° with acetic plus sulfuric acid, gave "terpinene" (b.p. 175-180°, hence the mixture of α- and γ-terpinenes), and a small amount of isofenchyl acetate.[625] The last ester was considered as the intermediate probably responsible for the terpinenes, but the authors are inclined to consider the presence of this acetate as incidental to a formation of α-fenchene, giving cyclofenchene or even δ-fenchene.



l-β-Pinene, heated with benzoic acid at temperatures "below 145°," gave α-pinene without bornyl esters.[19] However, bornyl benzoate, *l*-limonene, and *l*-α-pinene were formed at 125°,[21] and 14 per cent of bornyl benzoate accompanied the α-pinene formed at 125-130°.[20] Moreover, β-pinene, when treated with "organic acids" at 140-150°, led to α-pinene

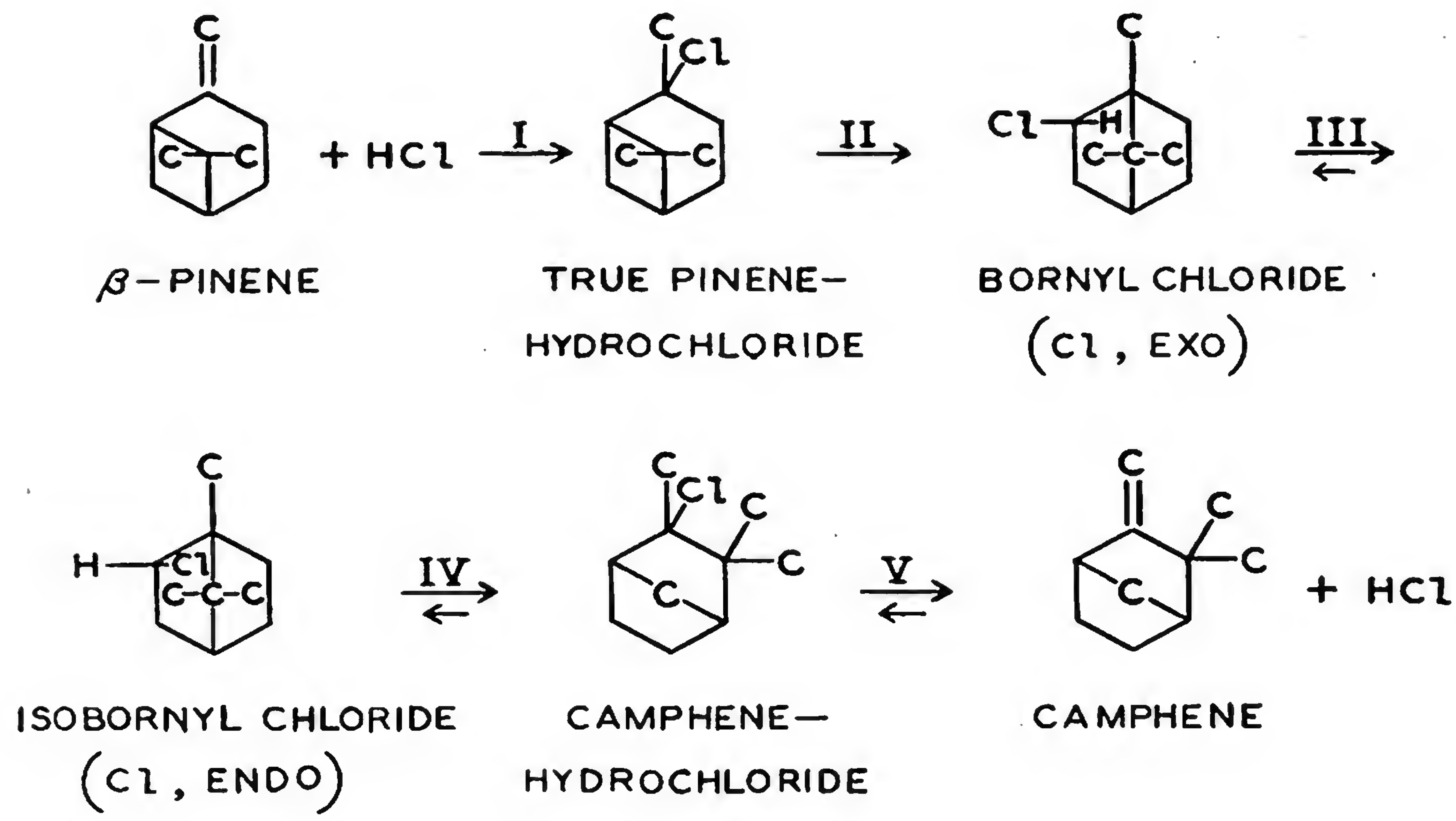
plus bornyl and isobornyl esters.[18] Treatment of *l*-β-pinene at 160° for 12-20 hours with salicyclic acid, which is a considerably stronger acid, gave 50 per cent of terpenes, consisting of limonene, *l*-α-pinene and "terpinene," and 35-36 per cent of bornyl esters.[19] The use of trichlorophenol for 30 hours at 145° resulted in a large conversion into *l*-α-pinene, along with traces of bornyl and fenchyl esters.[19] The conversions were formulated as follows:[19]



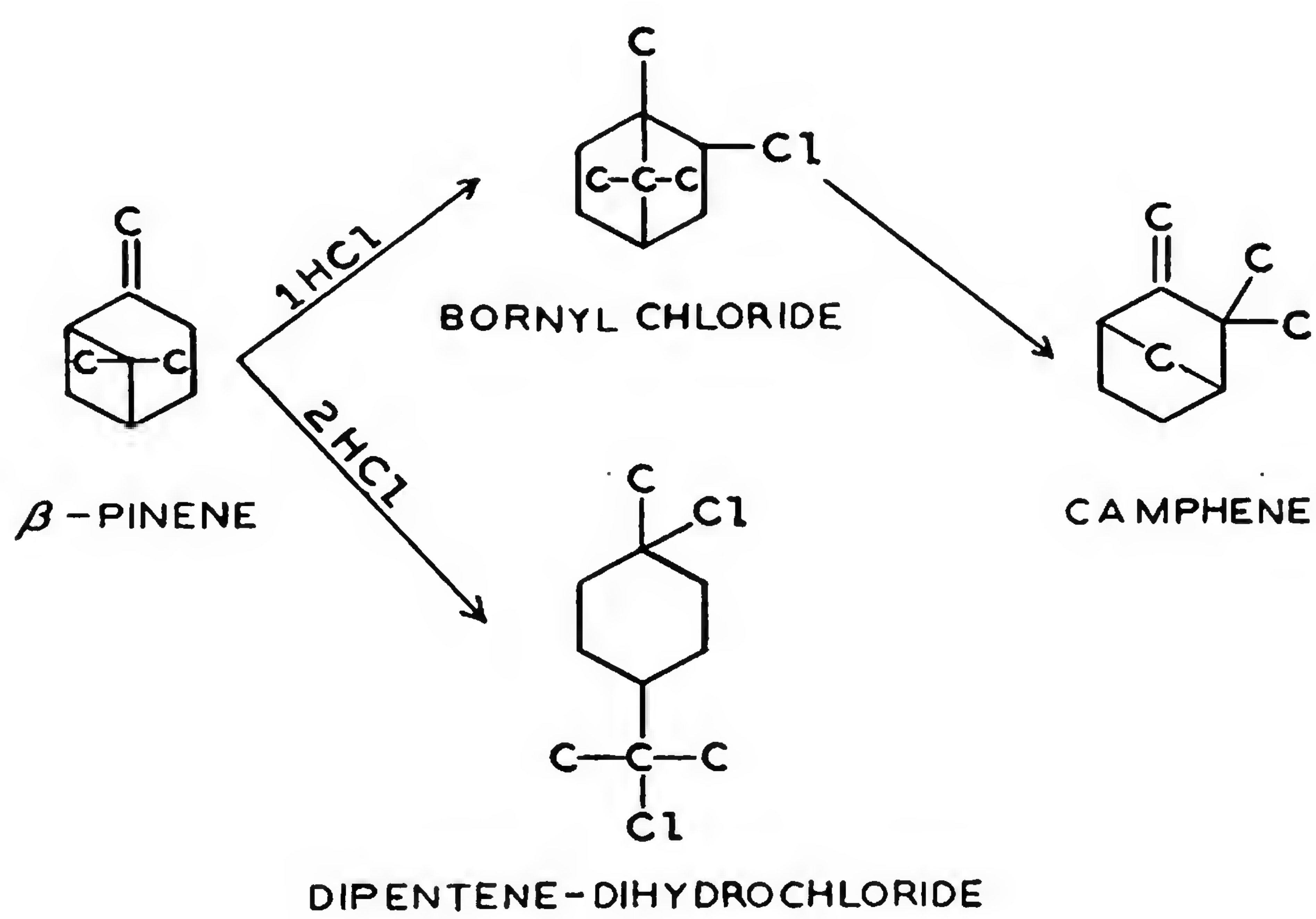
Some related preliminary work on β-pinene plus picric acid has been reported also.[322] *l*-β-Pinene, picric acid, plus benzene at 120° gave *l*-camphene, *l*-limonene, *l*-α-pinene, and 4 esters.[133] *l*-β-Pinene, heated 30 hours either with stearin at 145° or with colophony at "160-100°," yielded 70 per cent of *l*-α-pinene.[20]

l-β-Pinene, heated at 130-180° for 10 or 20 hours with abietic acid, formed camphene and *l*-α-pinene.[19] The formation of camphene from β-pinene, an "unusually delayed isomerization" via acids, involves a double Wagner rearrangement: that of β-pinene into bornyl esters[625] and of isobornyl into isocamphanyl esters.[369, 370] With hydrogen chloride, the first step is the formation (at −15°) of the exceedingly unstable true pinene-hydrochloride.[17] The latter isomerizes quickly (at 10°) into the relatively stable bornyl chloride.[370] Bornyl chloride, heated at 100°, undergoes a transformation into its less-stable stereoisomer, isobornyl chloride.* Still higher temperatures (125°) convert the isobornyl chloride into camphene hydrochloride, which is an isocamphanyl ester noted for its ready dissociation into camphene and hydrogen chloride[369, 370] The general reversibility of this system of chlorides decreases in the direction camphene to β-pinene. Camphene hydrochloride dissociates readily[39] into camphene and hydrogen chloride, whereas true pinene-hydrochloride quickly and irreversibly forms bornyl chloride.[17, 370] The transformation of β-pinene into camphene, via acids and acidic catalysts, proceeds apparently in 5 steps, according to the following "right-shift" of reactions:

* The Wagner rearrangements require the chlorine atoms of bornyl chloride and isobornyl chloride to be located respectively *exo* and *endo* to the opposite side of the non-planar or partly collapsed hexagon. These structural arrangements bring the chlorine atom of true pinene-hydrochloride and of bornyl chloride into actual proximity to the dimethylmethylene bridge and similarly place the chlorine atoms of isobornyl chloride and camphene hydrochloride in an advantageous mid-position. The present assignment is in agreement with that of Bredt[69a, 71a, 88a, 353b, 355a, 355b] and contrary to the proposals of Vavon and others.[2a, 2b, 15a, 15b, 257c, 258a, 319a, 609b, 609c]



l-β-Pinene, treated in the cold with dry ether (or acetic acid) saturated with hydrogen chloride, gives a mixture of *l*-bornyl chloride and dipentene dihydrochloride.[625] Bornyl chloride yields camphene when heated at 190-200° for 4 hours with anhydrous sodium acetate and acetic acid in a bomb tube.[617, 625]



The isomerizations of bicyclanes with unsaturated side-chains are given in Table 21, p. 310.

Conclusions

1. Bicyclanes with unsaturated side-chains isomerize to the following products: alkatrienes, alkenyl cyclenes, cyclodienes, isomeric bicyclanes with unsaturated side-chain and with same ring sizes, bicyclanes with unsaturated side-chain and different ring sizes, bicyclenes with same ring sizes, or bicyclenes with different ring sizes.

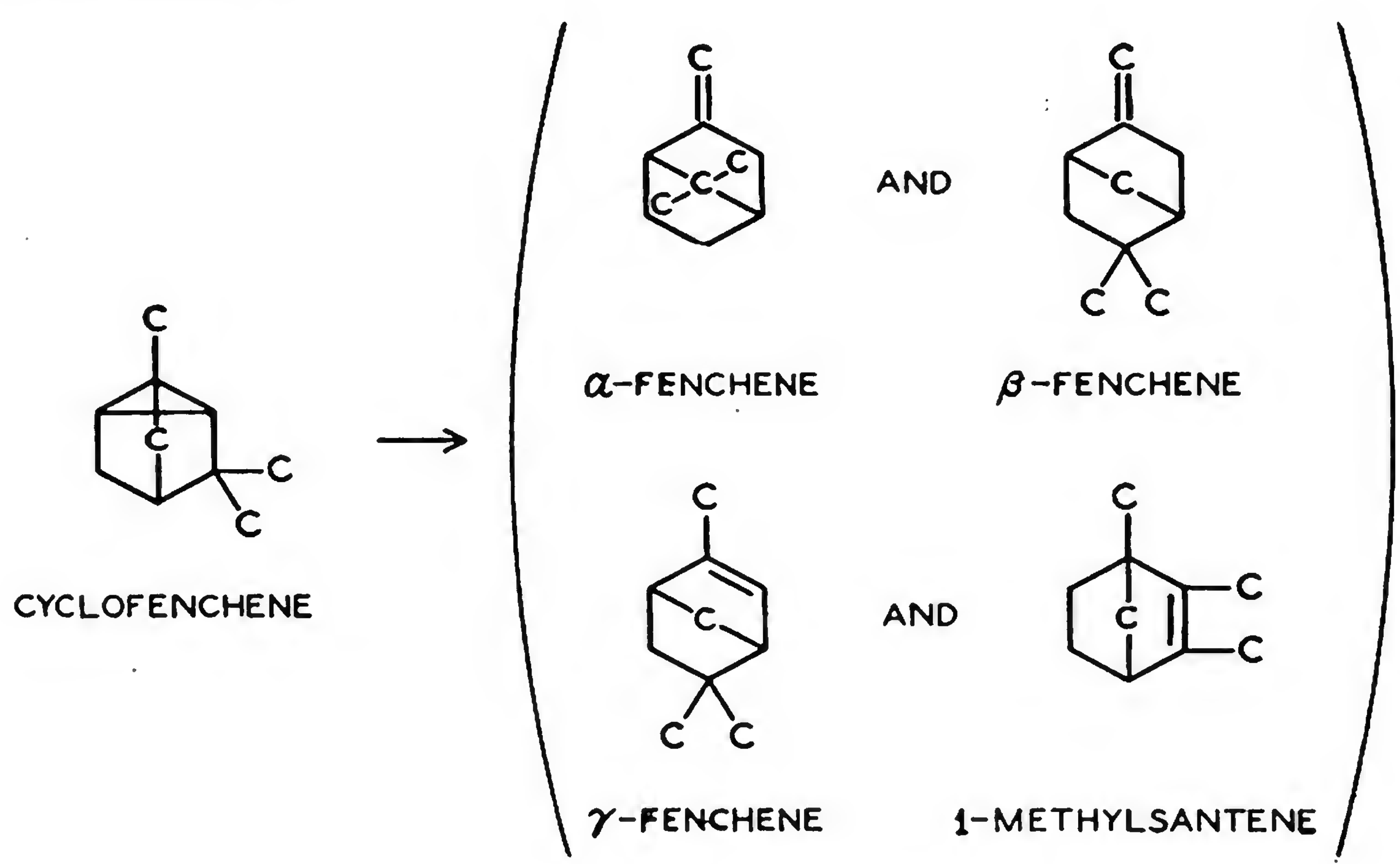
2. Formation of a cyclodiene involves both decyclization and a shift of side-chain double bond into the remaining ring.

3. Formation of a bicyclene, from β-pinene, is an easy, more-or-less direct, transformation proceeding even at room temperature, whereas the formation of an isomeric bicyclane with unsaturated side-chain (camphene) should be considered as a complex process.

TRICYCLANES

Isomerizations

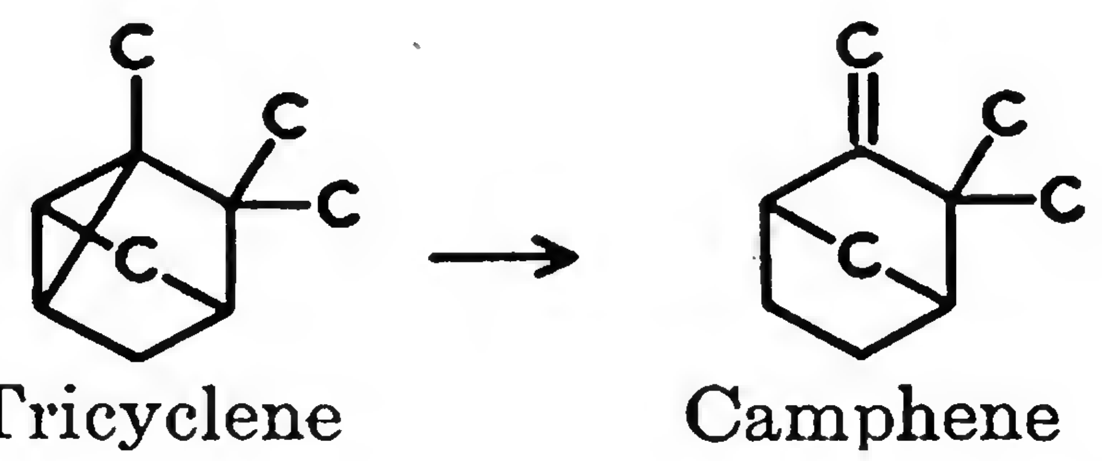
1,3,3-Trimethyl-tricyclo[2.2.1.0 2, 6]heptane (the tricyclic * terpene "cyclofenchene") isomerizes by rupture of one of 3 bonds comprising a cyclopropane ring, with formation of α-, β-, and γ-fenchenes and 1-methylsantene. An isomerization into α- and β-fenchenes occurred in the presence of platinized charcoal at 300°.[669] Heating of cyclofenchene with potassium acid sulfate or phthalic anhydride gave β- and γ-fenchenes,[320] whereas concentrated phosphoric acid[320] and activated "Florida earth"[587] formed 1-methylsantene (*i.e.*, 1,2,3-trimethylnorcamphene-2). The formation of 1-methylsantene[588] can be looked upon as a "retropinacol rearrangement," which occurs in preference to formation of δ-fenchene. The formation of β- and γ-fenchenes, as a pair of products, calls for the presence of 2,7,7-trimethylnorcamphene-2 whenever α-fenchene is formed. However, neither 2,7,7-trimethylnorcamphene-2 nor 5,7,7-trimethylnorcamphene-2 (another possibility) has been reported to date:



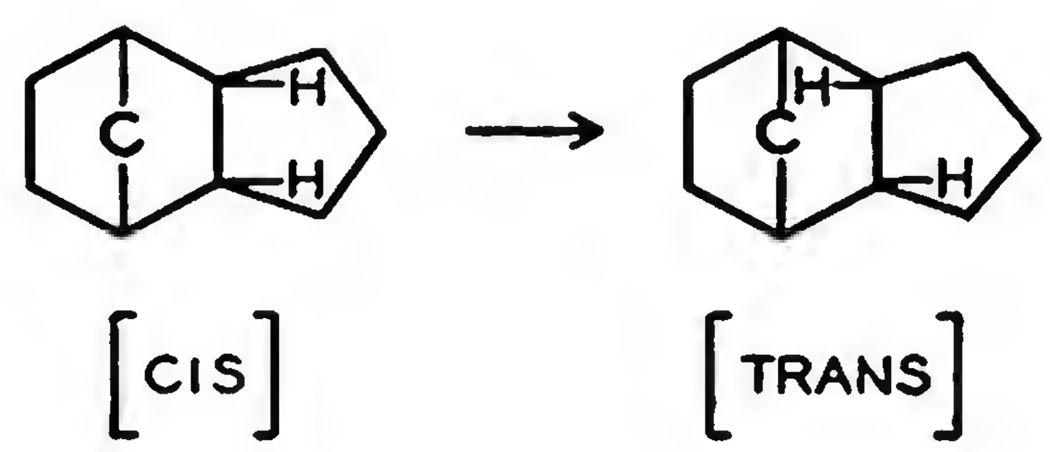
2,3,3-Trimethyl-tricyclo[2.2.1.0 2, 6]heptane (the tricyclic terpene "tricyclene") isomerizes to *dl*-camphene by rupture of one bond and migration of a hydrogen atom. This isomerization occurred both upon heat-

* The "cyclohexane" rings of cyclofenchene, tricyclene, and tetrahydro-di-cyclopentadiene are not to be construed as established or additional rings. They are assumed to be physically non-existent and to be adequately defined as two cyclopentane rings of fused type.

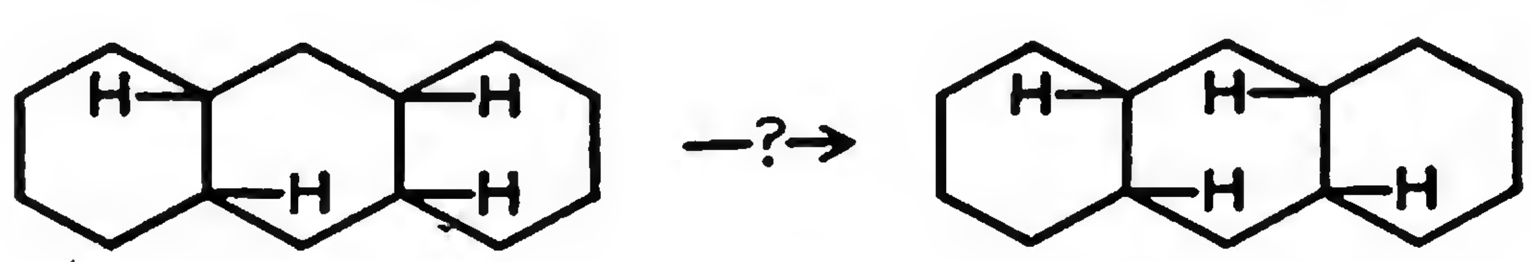
ing with sodium hydrogen sulfate at 168° [355] or upon passage over nickel at 180-200° in a slow current of nitrogen.[369]



Tricyclo[5.2.1.0^{2,6}]decane (*i.e.*, tetrahydro-di-cyclopentadiene) probably exists in *cis* and *trans* forms.[162] Unfortunately, structural errors are to be found in the literature, due to a prolonged controversy over the constitution of "dicyclopentadiene." [157] Long heating of tricyclodecane (m.p. 77°) with sulfuric acid containing a small amount of pyrosulfuric acid, at a temperature somewhat above 77°, gave a stereoisomer of m.p. 9°.[162] This isomerization may be formulated as a conversion of the *cis*-tricyclodecane into its *trans* form:

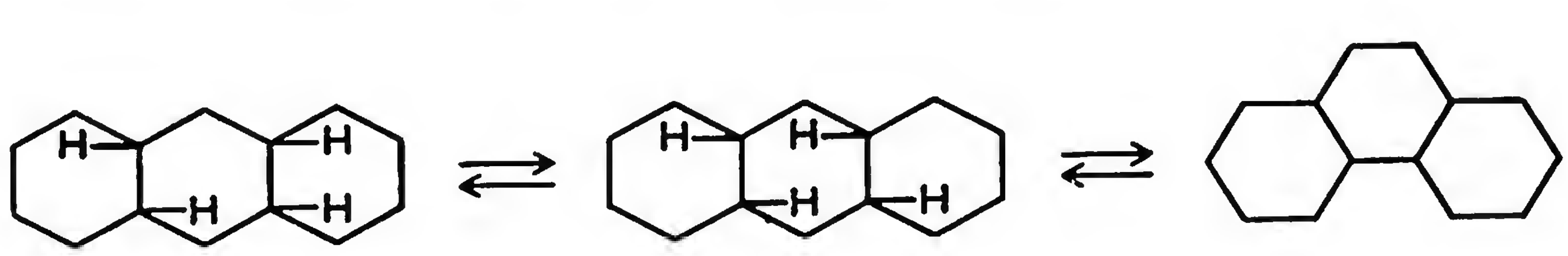


Prolonged heating of "liquid" tetradecahydroanthracene at 270° in the presence of nickel and hydrogen under high pressure gave "solid perhydroanthracene." This is apparently an isomerization of a labile liquid form and may be a conversion of 3,8-*cis*-1,10-*trans*-tricyclo-[8.4.0.0^{3,8}]tetradecane into 1,10-*trans*-3,8-*trans*-tricyclotetradecane:[637]



A similar reaction occurred when "liquid" tetradecahydroanthracene was treated at 100° with aluminum chloride, or with molybdenum trisulfide under hydrogen pressure at 330-380°.[451]

"Solid" tetradecahydroanthracene plus compressed hydrogen formed some tetradecahydrophenanthrene when heated at 460° with or without molybdenum trisulfide, whereas treatments with aluminum chloride at 100° without hydrogen probably gave mixtures of "liquid" tetradecahydroanthracene plus tetradecahydrophenanthrene:[451]



Tetradecahydrophenanthrene was converted partly into "solid" tetradecahydroanthracene when subjected either to aluminum chloride at 100° or to molybdenum trisulfide and hydrogen under pressure at 380°.[451] Tetradecahydrophenanthrene is a tricyclo[8.4.0.0^{4,9}]tetradecane with interesting stereochemical possibilities.[352]

Isomerizations of tricyclanes are given in Table 22, p. 316.

Conclusions

1. The isomerizations of cyclofenchene and tricyclene indicate that cyclopropane rings (comprising a part of tricyclanes) can be expected to open readily. The products formed are bicyclanes with an unsaturated side-chain, or bicyclenes.
2. The isomerization of tricyclanes from *cis* into *trans* forms can be expected on account of their close relationship to the saturated bicyclanes.

PENTACYCLANES

l-α-Cryptomerene, obtained from the Cryptomeria japonica, is a diterpene ($C_{20}H_{32}$) of unknown structure. Treated with anhydrous hydrogen chloride in the presence of well-cooled ether, it gives β-cryptomerene.[601] These isomers can be considered as pentacyclanes, since neither combines with hydrogen chloride or iodine.[601]

Chapter V

Cyclenes, Bicyclenes, and Polycyclenes

The isomerizations of cyclenes, bicyclenes, and polycyclenes (*i.e.*, the cycloölefins) are discussed in the following order: cyclenes and cyclenes with saturated side-chains, cyclenes with unsaturated side-chains, cyclodienes with saturated side-chains, cyclodienes with unsaturated side-chains, bicyclenes and bicyclenes with saturated side-chains, bicyclenes with unsaturated side-chains, bicyclodienes with saturated side-chains, tricyclenes and tricyclenes with saturated side-chains, tricyclenes with unsaturated side-chains, tetracyclenes, and pentacyclenes.

The isomerizations of the cyclenes contain several examples in the sesquiterpene group $C_{15}H_{24}$, wherein structures of many members are unknown. The concept of molecular refraction, and of its exaltation due to the influence of conjugated double bonds, has been of value in elucidating structures of the sesquiterpenes.[490] These concepts should be used more often in the entire cyclene series of hydrocarbons. The sesquiterpenes include aliphatic members with 4 double bonds, monocyclics with 3 double bonds, bicyclics with 2 double bonds, tricyclics with one double bond, and possibly saturated tetracyclics. Usually, these members occur as a mixture in which the double bond is unlocated. The isomerization of the aliphatic sesquiterpenes has been discussed in Chapter II, under "Alkapolyenes."

Typical examples of isomerization among the diterpenes ($C_{20}H_{32}$) are the conversions of α-camphorene, phyllocladene, and sclarene into isomers. The diterpenes theoretically comprise aliphatic, and monocyclic to pentacyclic members, all of which can be considered as isoprene tetramers, each of which has a different degree of cyclization. Isomerization of these members consists usually of alterations in both degree of cyclization and location of double bonds. Variation of the size of rings, aromatization, and transformations in the side-chain are still other types of isomerization possible in diterpenes. Again, the known structures of the terpenes, sesquiterpenes, and diterpenes, as isoprene polymers, further suggest a possible partial depolymerization followed by recombination to an isomer.

The isomerization mechanisms of cyclenes will be discussed for members having special characteristics due to their structures or reaction conditions. Explanations of isomerization that have been given in pre-

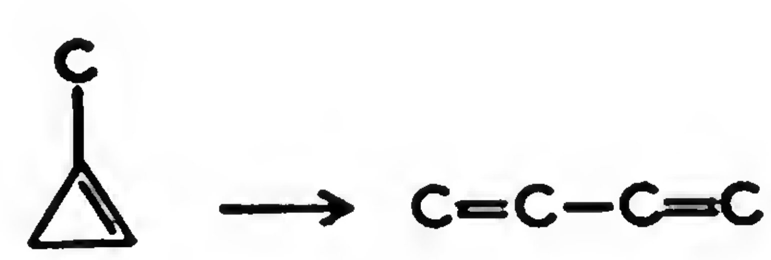
ceding sections are generally applicable to movements of double bonds, cyclization and decyclization occurring within the various cyclenes.

Cyclenes and Cyclenes with Saturated Side-Chains

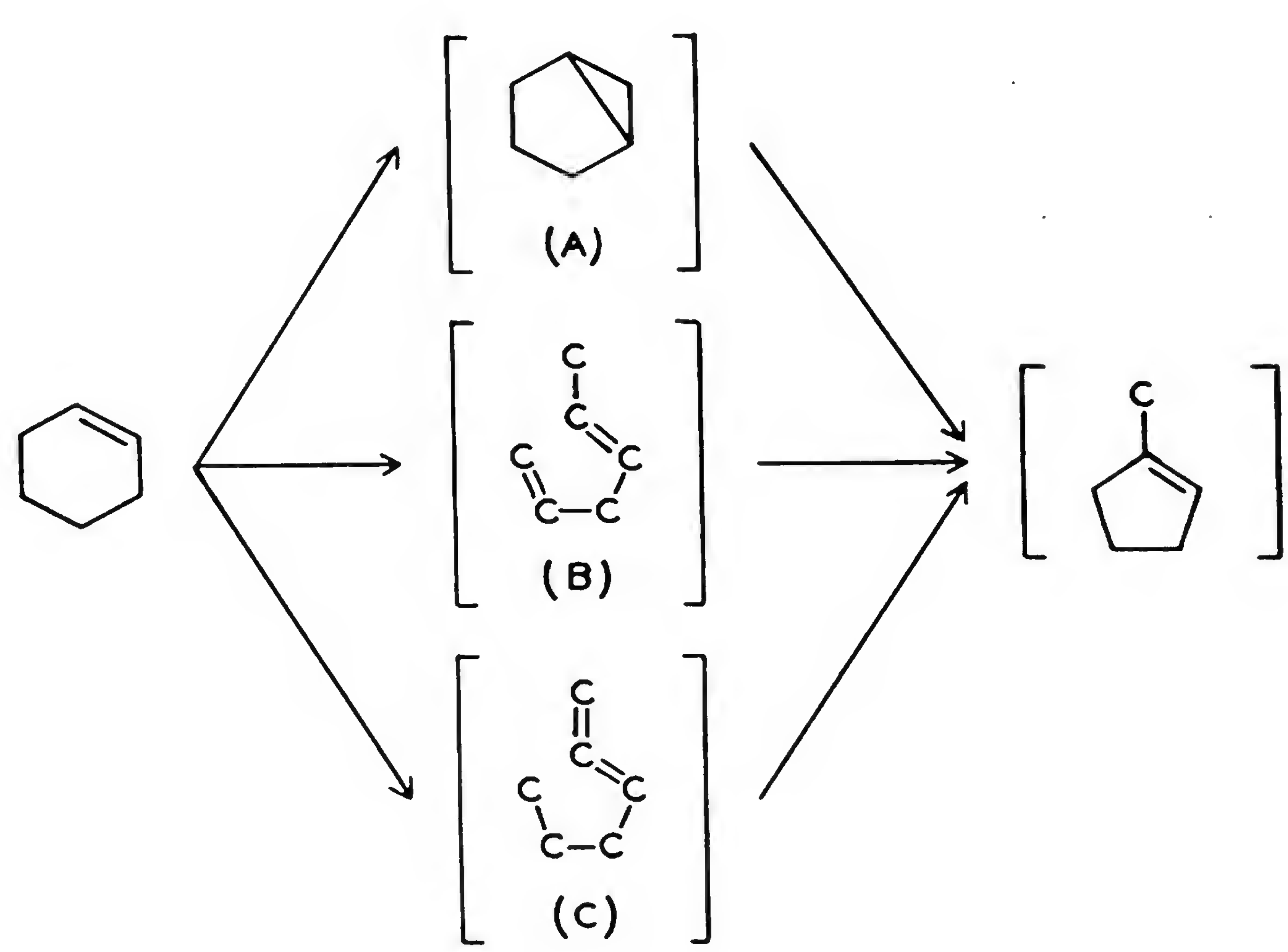
The cyclenes with saturated side-chains or without side-chains comprise the simplest group of all cyclenes. Nevertheless, only a few examples of isomerization in this group are known. The movement of saturated side-chains *per se* has not been observed, which may be due to the possible existence of equilibria favoring: shifts of the double bond, decyclization, or decyclization plus cyclization.

Isomerizations

1-Methylcyclopropene-1, passed over alumina at 325°, gave butadiene-1,3.[373] The product contained isobutene, originally present in the 1-methylcyclopropene-1.



Cyclohexene passed once over silica gel at 400° or 450°, or twice over heated alumina, formed "methylcyclopentene."[665] Isolation of methylcyclopentane, when the catalyzate was subjected to (a) hydrogenation, (b) selective dehydrogenation of the cyclohexane, and (c) elimination of benzene, was given as indirect evidence of isomerization. These experiments do not prove that methylcyclopentenes were present in the catalyzate to the exclusion of methylenecyclopentane. Bicyclo-[3.1.0]hexane (A) was proposed as an intermediate product, but hexadienes (B) (C) are also possible intermediates:



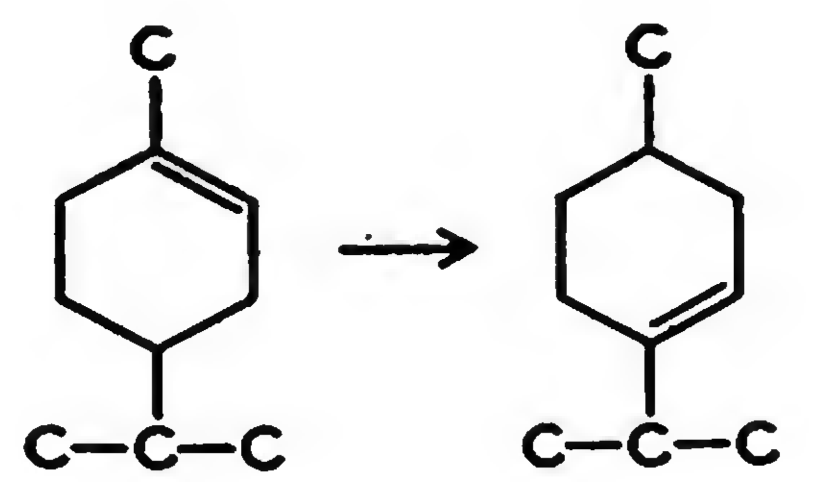
The passage of cyclohexene over a phosphoric acid-on-silica catalyst at 350° yielded about 64 per cent of a "methylcyclopentene."[529a]

Conduction of cyclohexene over titanium dioxide, at 350° followed by re-treatment of the main condensate, or singly at 400° or 450°, gave about 19, 18, and 11 per cent, respectively, of "methylcyclopentene."[12a] Passage of cyclohexene over beryllium oxide at 450°, with one recycle of the condensate's main fraction, yielded approximately 48.2 per cent of "methylcyclopentene."[12a] The four preceding "methylcyclopentene" percentages are based upon the final yields of methylcyclopentane obtained from the stated cyclohexene plus "methylcyclopentene" fractions by (a) hydrogenation over platinized charcoal at 150° to form cyclohexane plus methylcyclopentane, (b) selective dehydrogenation of the cyclohexane over the same catalyst at 300°, giving a benzene plus methylcyclopentane mixture, and (c) elimination of benzene by treatment with fuming sulfuric acid. "Methylcyclopentene" has been suggested as one intermediate in the pressure hydrogenation of cyclohexene over molybdenum disulfide (MoS_2), since some methylcyclopentane accompanies the cyclohexane formed.[408a]

1-Methylcyclohexene-1, heated with a mixture of quinoline and quinoline-hydriodide, gave only 2.5 per cent of methylenecyclohexane.[181]

4-Methylcyclohexene-1 (*i.e.*, 1-methylcyclohexene-3) was probably converted into "dimethylcyclopentene" when passed over silica gel at 450°, according to the insufficient evidence afforded by isolation of heptanes (b.p. 85.0-93.0°/741 mm. Hg, $D_4^{20} = 0.6891$, $n_D^{20} = 1.3900$) after the catalyzate was subjected to (a) hydrogenation, (b) dehydrogenation of methylcyclohexane, and (c) removal of toluene.[665] This experiment also did not prove that dimethylcyclopentenes were present in the catalyzate to the exclusion of 1-methyl-(2 or 3)-methylenecyclopentanes.

1-Methyl-4-isopropylcyclohexene-1 (*i.e.*, menthene-1 or carvomenthene) when passed as a vapor at 300-450° over bleaching earth, pumice, silica gel, the zeolite-like "tonsil," or a metal salt (such as magnesium sulfate or copper phosphate) yielded over 50 per cent of 1-isopropyl-4-methylcyclohexene-1 (*i.e.*, 1-methyl-4-isopropylcyclohexene-3; menthene-3 or menthomenthene):[501, 521]



d-1-Methyl-4-isopropylcyclohexene-3 was partly racemized when boiled for 24 hours with alcohol containing *p*-toluenesulfonic acid.[258]

The reaction, however, can be used for the quantitative analysis of *d*-1-methyl-4-isopropylcyclohexene-2 and *d*-1-methyl-4-isopropylcyclohexene-3 mixtures, since the first hydrocarbon is much more slowly racemized.[258a] Pending further investigations, the course of the main racemization can be considered as formation of the optically inactive ester of menthanol-4 and subsequent subtraction of *p*-toluenesulfonic acid.

d-1-Methyl-4-isopropylcyclohexene-3 formed "cyclopentene hydrocarbons" when passed twice over silica gel at 375°, 400°, or 450°.[666] "Cyclopentane hydrocarbons" were isolated after the catalyzates were subjected to (a) hydrogenation, (b) selective dehydrogenation, and (c) elimination of *p*-cymene. It was suggested that the isomers are di- or tri-substituted cyclopentenes whose presence requires intermediary substituted bicyclohexanes. These experiments do not prove that "cyclopentene hydrocarbons" were present to the exclusion of (mono- or di-alkyl)-alkenyl cyclopentanes as isomers.

The isomerizations of cyclenes and cyclenes with saturated side-chains are given in Table 23, p. 318.

Conclusions

1. The double bond of cyclenes with saturated side-chains can shift into a new position in the ring and probably also into a side-chain.

2. The cyclopropene ring can be expected to decyclize, giving an alkadiene.

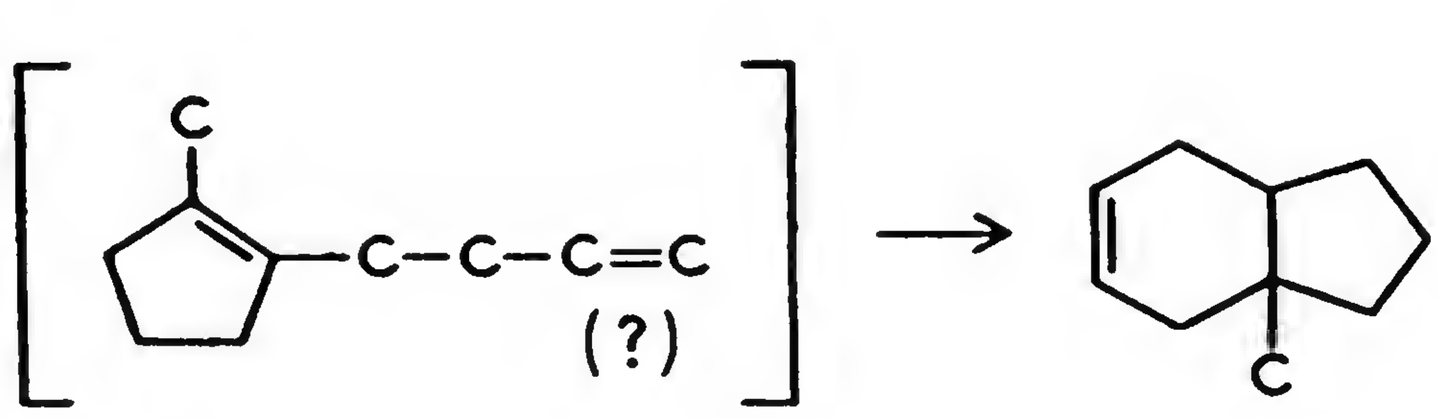
3. Cyclohexene rings probably form cyclopentenes in some cases, possibly via alkadienes.

Cyclenes With Unsaturated Side-Chains

Isomerizations

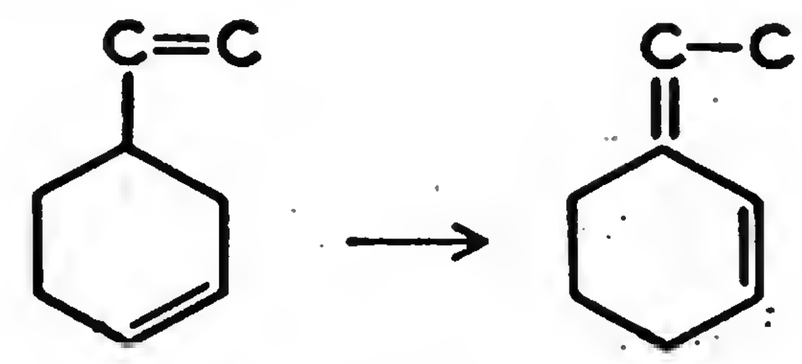
The cylenes with unsaturated side-chains belong to a hydrocarbon group wherein individual members have the ability to isomerize into several products. Their reactivity is chiefly due to the unsaturated side-chain, which can undergo shifts of the double bond or can cause further cyclization into bicyclic hydrocarbons.

Treatment of 1-methyl-2-(3-butenyl)cyclopentene-(1?) with phosphoric acid plus phosphorus pentoxide resulted largely in a cyclization to 3a-methyl-3a,4,7,7a-tetrahydroindan:[170]



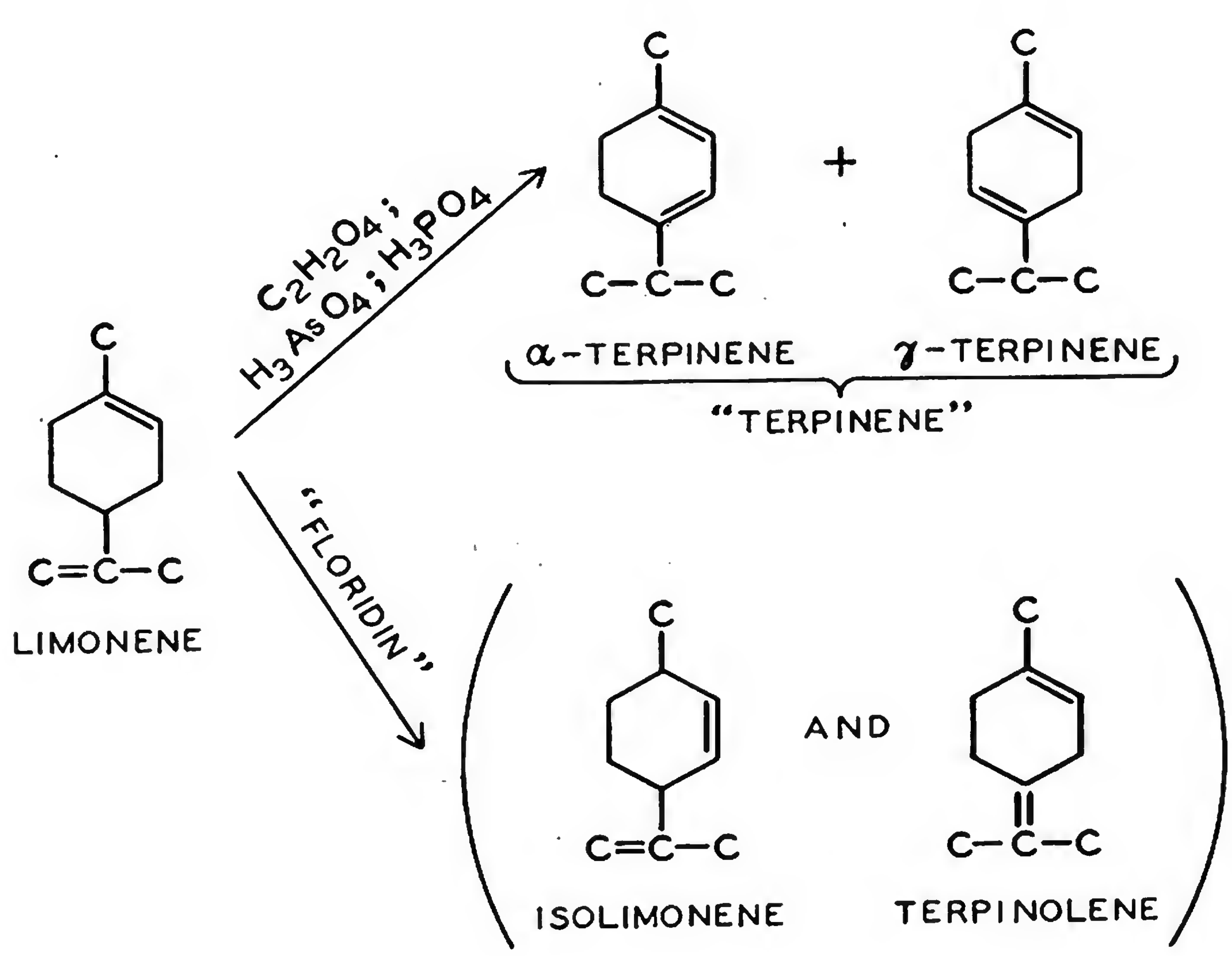
Probable Structure[170]

1-Vinylcyclohexene-3 isomerized to 1-ethylidenecyclohexene-2 at 200-235° in the presence of "Floridin."[550] In this reaction, both double bonds move to form a conjugated system:



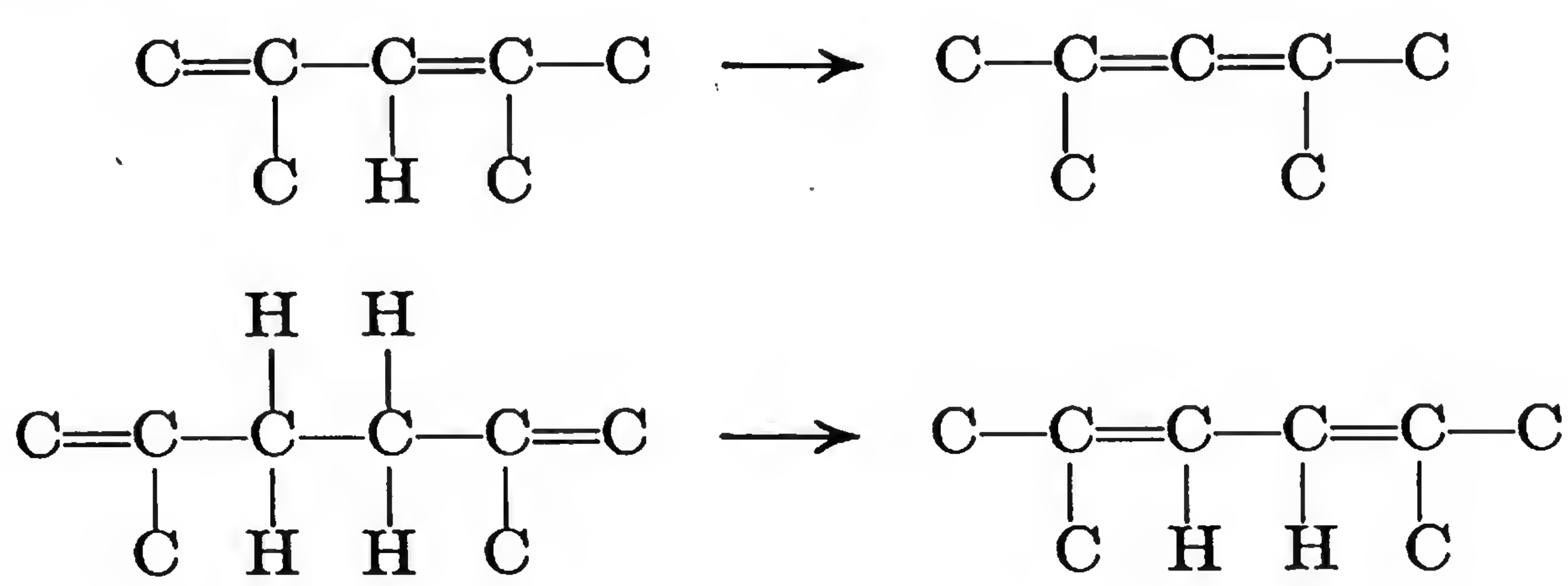
Optically active 1-methyl-4-isopropenylcyclohexene-1 ("limonene" by definition) is "inverted" or racemized to dipentene (*dl*-limonene) when heated several hours at 250-270° [108, 615] or at 380°.[108] There are no effective catalysts for the racemization of limonene.[107]

d-Limonene formed a little α- and γ-terpinenes and much diterpene when treated with phosphoric acid at 22-32°;[103] α-terpinene was reported as the only isomer on heating limonene with anhydrous oxalic acid.[394] Limonene when heated under reflux with arsenic acid gave "terpinene,"[208, 209] but when passed over hot "Floridin," yielded 1-methyl-4-isopropenylcyclohexene-2 (isolimonene) and probably some 1-methyl-4-isopropylidenecyclohexene-1 (terpinolene).[550] There was no 1-methyl-4-isopropylidenecyclohexene-2 (isoterpinolene) among the products, probably due to its removal by polymerization. Dipentene, which is *dl*-limonene, was changed into "terpinene" and a polymer called "dipinene," when heated under reflux with fuller's earth for 1.5 hours.[610] Dipentene yielded considerably over 26 per cent of terpinolene and 12.9 per cent of polymers when heated at 170° for one hour with 0.5 per cent of activated Chasov-Jarsky clay.[480a] Further treatment of the product (polymer-freed and containing over 53 per cent of dipentene) for an hour with one per cent of the same catalyst resulted in the formation of 15.8

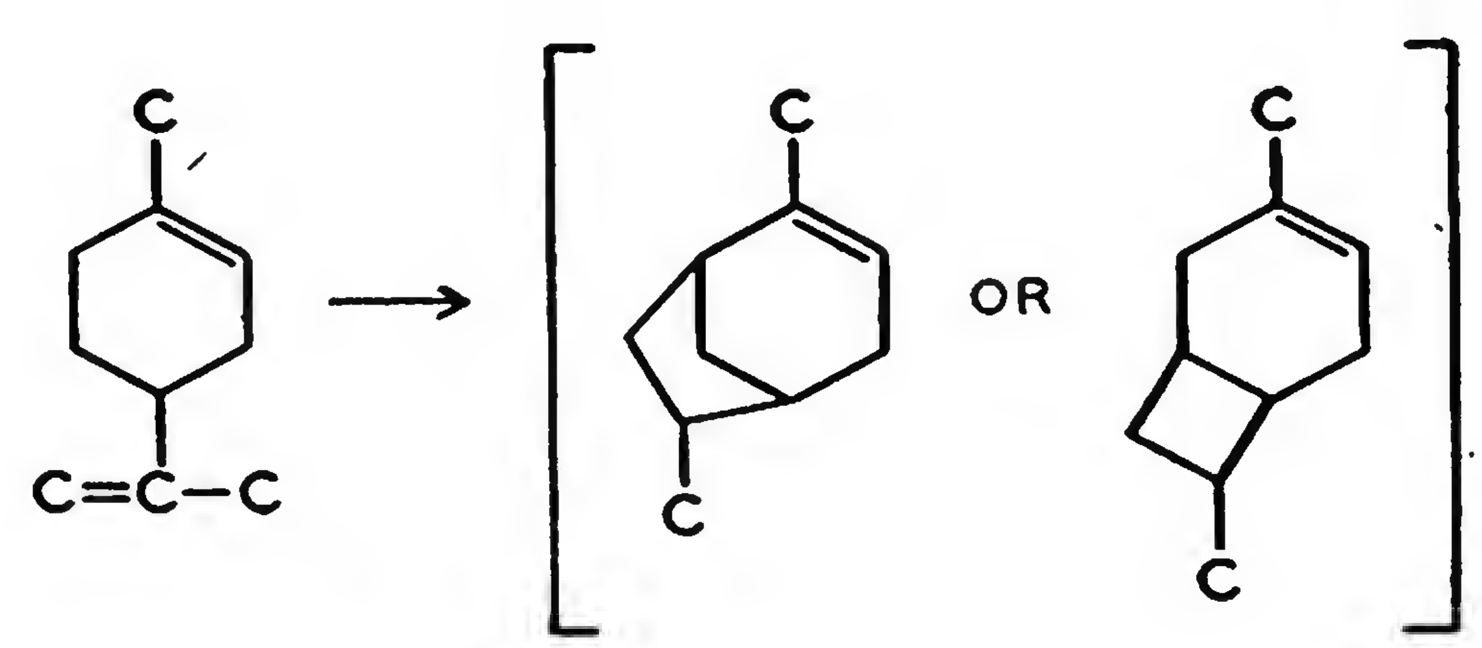


per cent of α-terpinene, presumably at the expense of part of the terpinolene. Four consecutive treatments of dipentene with the activated clay, however, led to the formation of menthene-3 and *p*-cymene, as terpene disproportionation products, and to much polymer.

It is of interest to note that in the isomerization to terpinolene, and possibly (transitionally) in the formation of "terpinene," the isopropenyl group of limonene becomes an isopropylidene group. This change is similar to the following aliphatic three-carbon isomerizations involving isopropenyl groups:

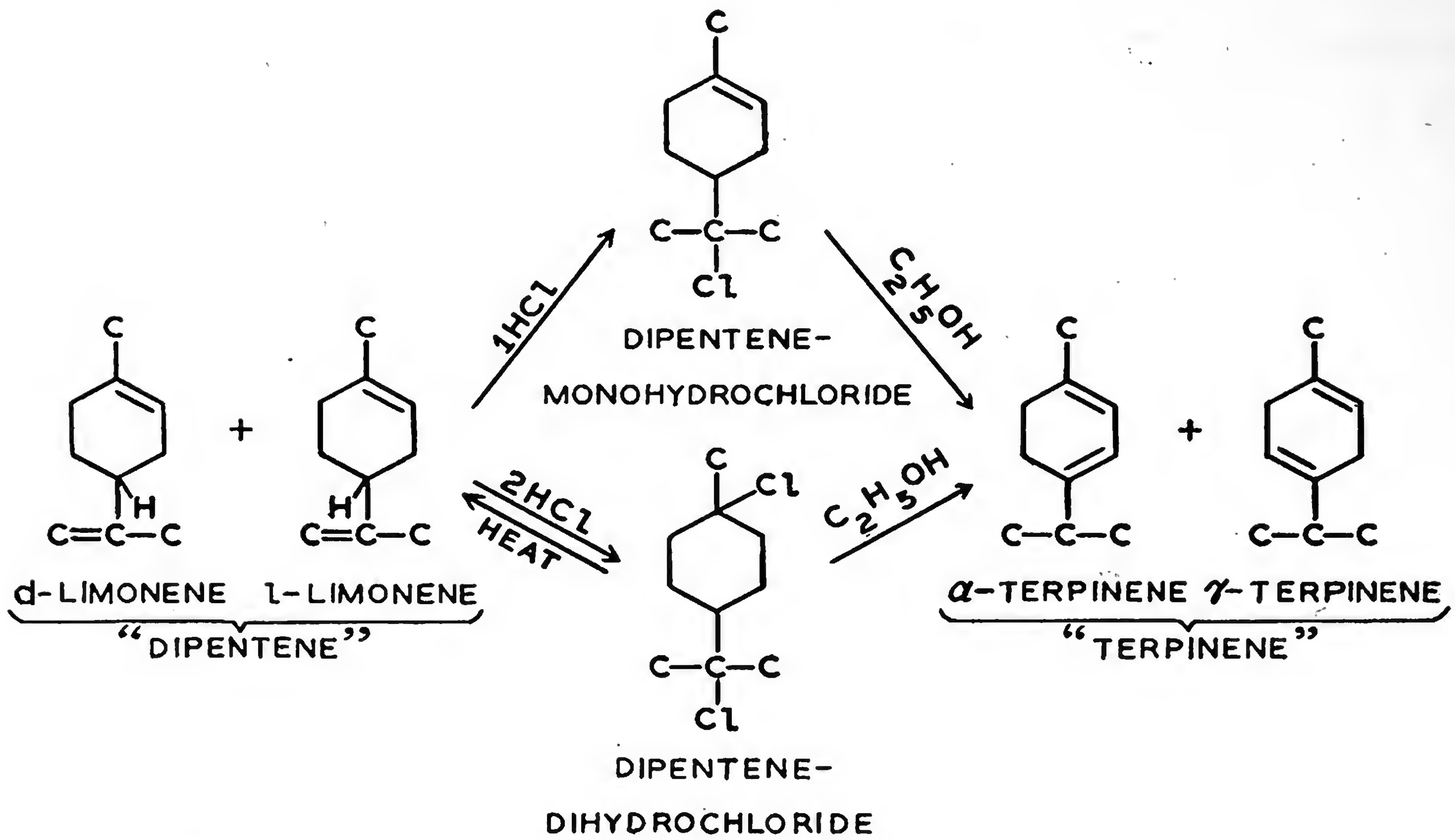


The isopropenyl group of limonene can also enter into cyclizations, yielding two isomeric bicyclic terpenes.[275a] The required conditions are passage of the limonene over a phosphoric acid on silica catalyst at 150-250°. The resulting isomers (b.p. 163-165°/750 mm. Hg, $D_4^{19} = 0.8416$, $n_D^{20} = 1.4630$; b.p. 169-171°/750 mm. Hg, $D_4^{20} = 0.8444$, $n_D^{20} = 1.4674$) are believed to be *cis* and *trans* forms of 2,6-dimethylbicyclo-[3.2.1]octene-2, or possibly of 3,7-dimethylbicyclo[4.2.0]octene-3:

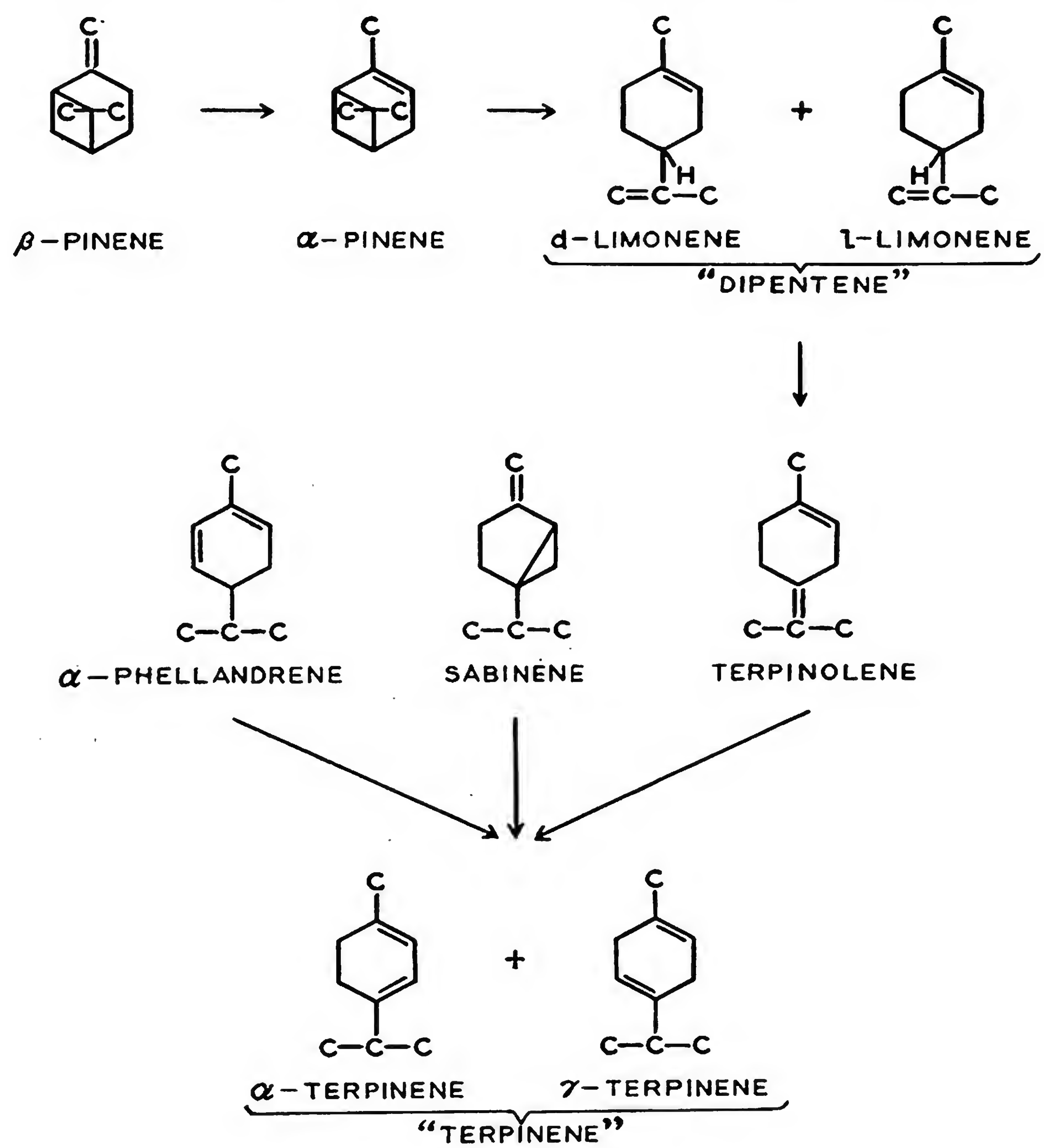


Hydrogenation of the two isomers under pressure in the presence of a nickel-kieselguhr catalyst yielded a bicyclane (b.p. 170.5/750 mm. Hg, $D_4^{27} = 0.8283$, $n_D^{20} = 1.4530$).

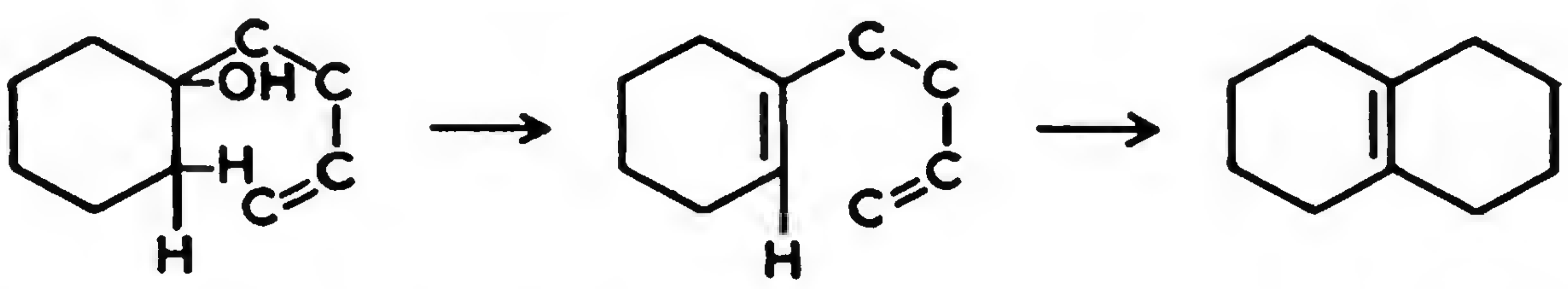
Dipentene (*dl*-limonene), treated for 1 hour with alcoholic sulfuric acid at 100°, formed "terpinene" and much resin.[617] Alcoholic hydrochloric acid is probably a catalyst also, since dipentene-dihydrochloride gave "terpinene" when heated under reflux for 3 hours with alcohol.[617] Dipentene-dihydrochloride heated for 3 hours under reflux, then steam-distilled, yielded a principal fraction containing dipentene;[616] this indicates an equilibrium state. Dipentene-monohydrochloride is an intermediate in the formation of "terpinene."[617, 618]



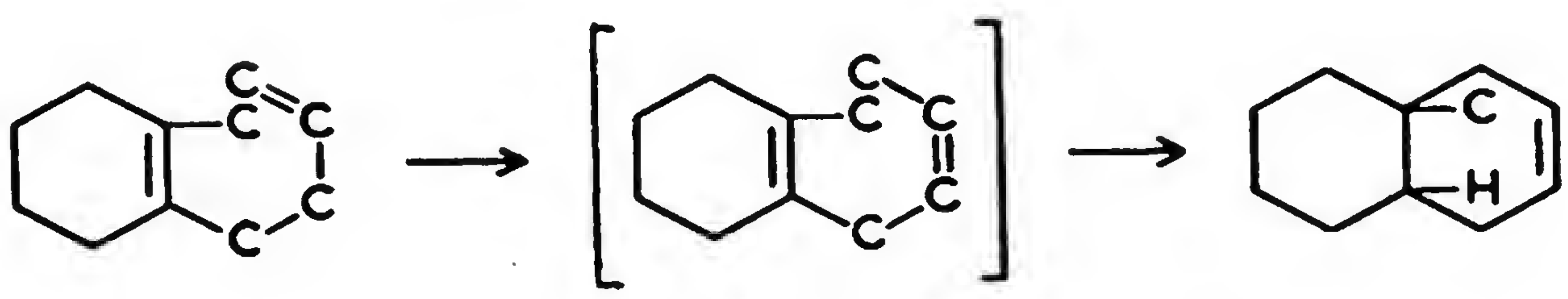
Terpinolene heated with acids gives "terpinene." [620] This isomerization is of considerable theoretical significance in terpene chemistry. The probable courses of terpene isomerizations yielding "terpinene" are:



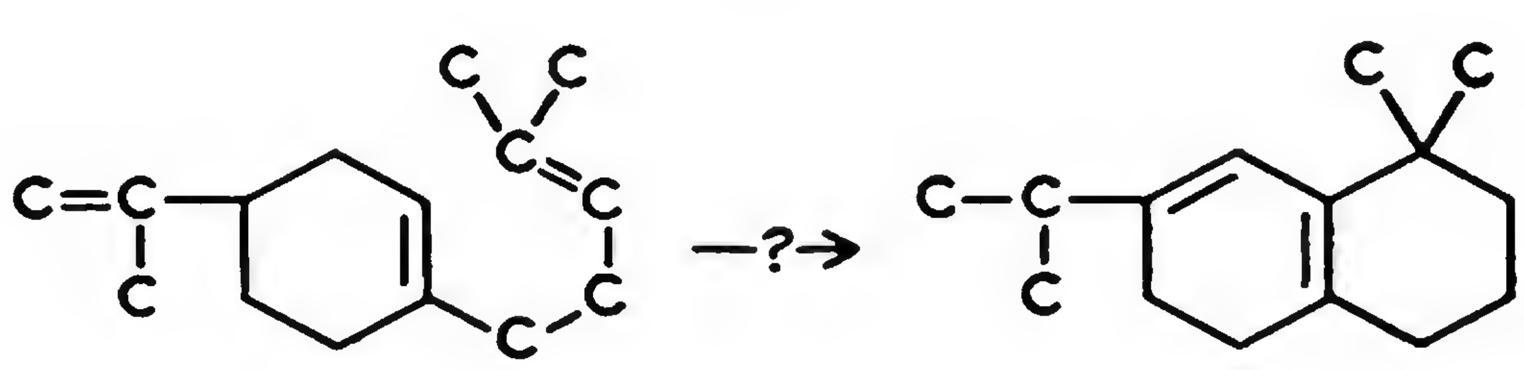
A mixture of 1-(3-butenyl)cyclohexene-1 and 1,2,3,4,5,6,7,8-octahydronaphthalene ($\Delta^{9,10}$-octalin) resulted when 1-(3-butenyl)cyclohexanol-1 was heated under reflux for 3 hours at 160° with phosphoric acid plus phosphorus pentoxide. The cyclization of the diene was completed by treatment of the hydrocarbon mixture with phosphorus pentoxide (30 per cent) for 3 hours at 140°.[353] This cyclization is analogous to the intermolecular dimerization of an alkene:



1-Methyl-2-(3-butenyl)cyclohexene-1, in the presence of phosphoric acid at 130°, formed *cis*-9-methyl-1,4,5,6,7,8,9,10-octahydronaphthalene.[253] The cyclization can be explained by assuming the formation of an intermediate, such as 1-methyl-2-(2-butenyl)cyclohexene-1:

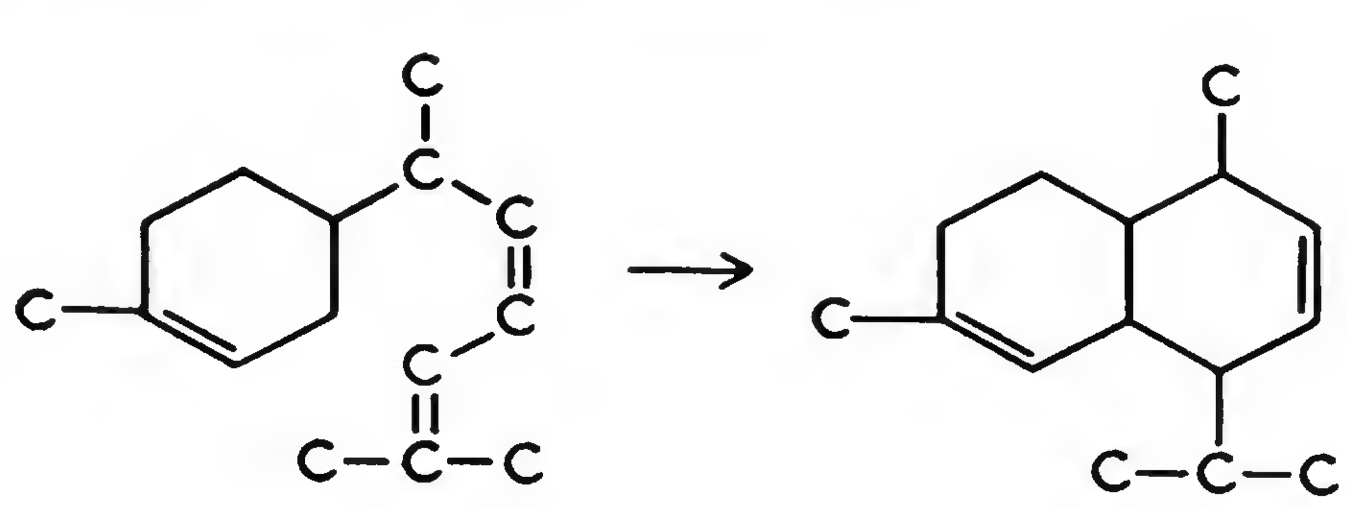


Cycloisoprenemyrcene, when heated at 100° for 10 hours and then at 120° for 2 hours with 85-per cent formic acid, was converted into 66.7 per cent of bicycloisoprenemyrcene.[484] This isomerization has been formulated tentatively as follows: [484]



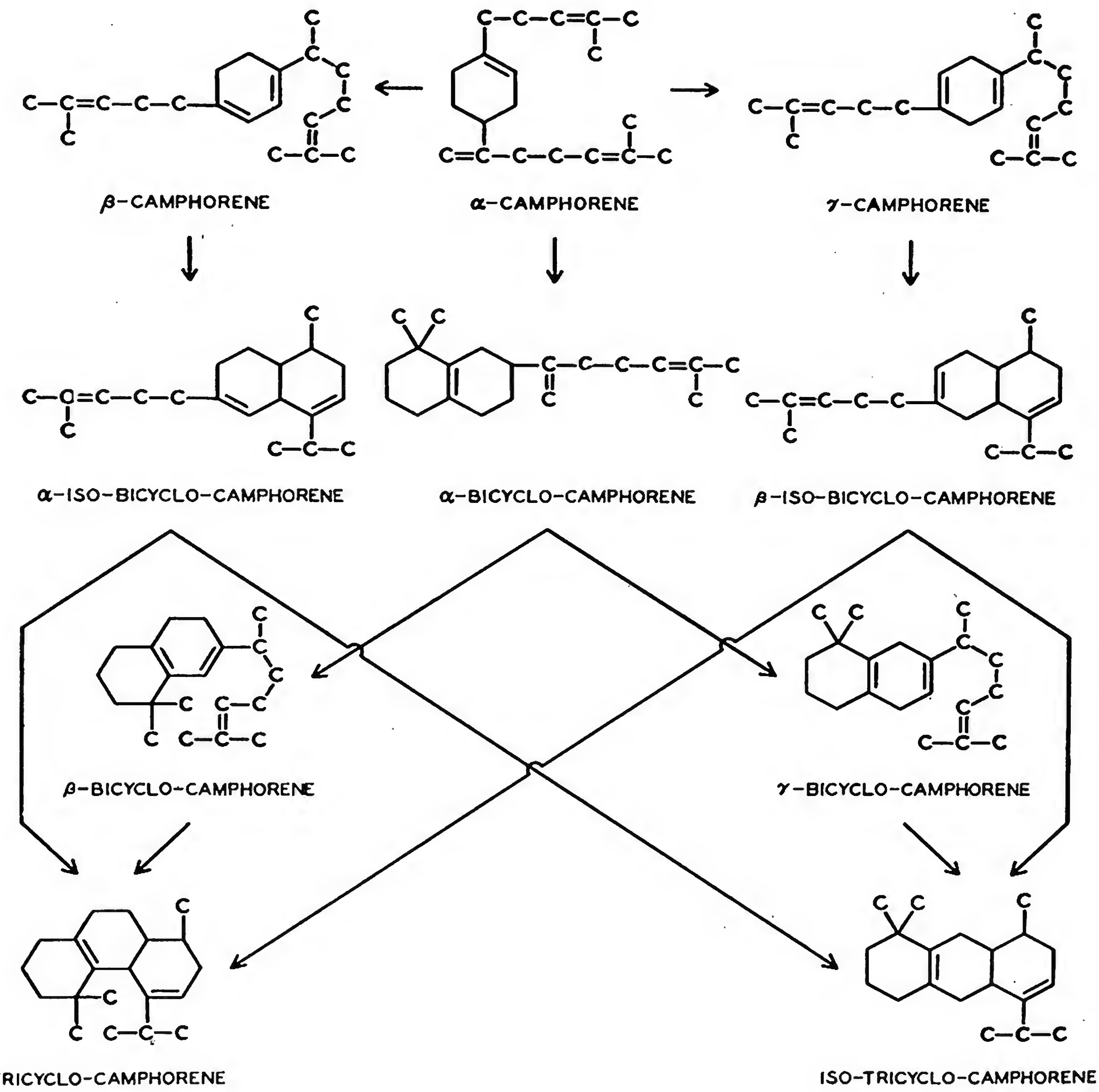
If one adopts Ruzicka and Stoll's system of nomenclature for the camphorenes,[494] then the above cyclization should be considered as that of α-cycloisoprenemyrcene into β-bicyclo-isoprenemyrcene.

l-Zingiberene, which is another monocyclic sesquiterpene, formed the bicyclic *l*-iso-zingiberene when treated for 6 hours at 60-65° with acetic acid containing diluted sulfuric acid [490, 495, 535] Since the structure of zingiberene is established, whereas that of iso-zingiberene is deducible from the product (cadalene) obtained in its dehydrogenation,[490] the cyclization may be formulated as follows:



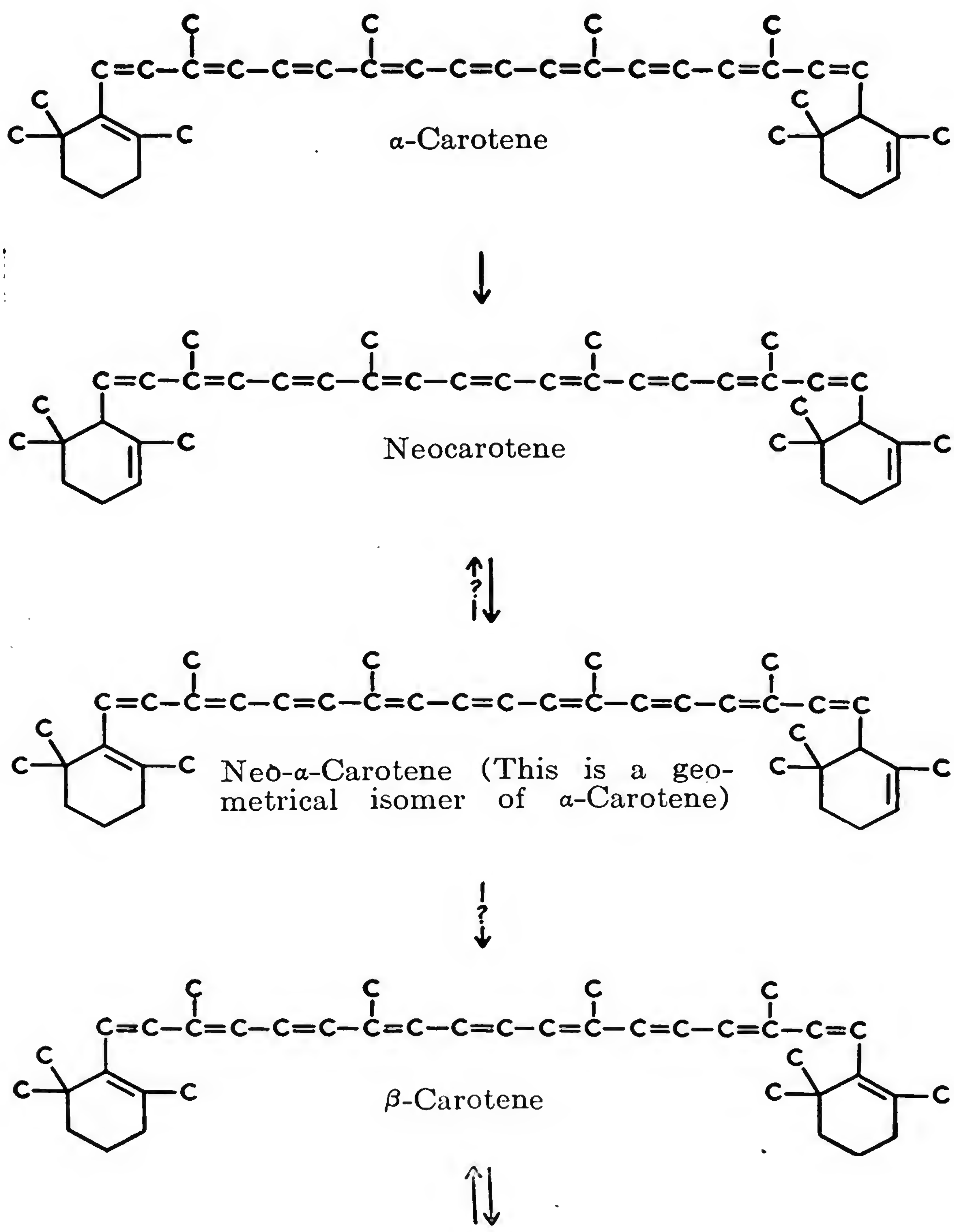
ZINGIBERENE ISO-ZINGIBERENE

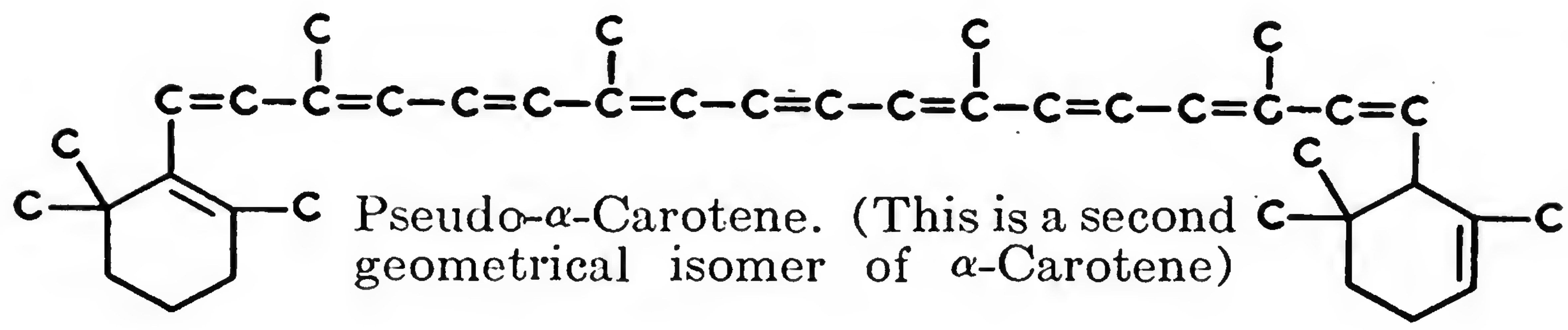
α-Camphorene, which is a monocyclic diterpene as well as the dimer of myrcene, gives a bicyclic isomer when heated (0.5 hour) with 95-per cent formic acid, but forms a tricyclic isomer upon a further 3 hours' heating with the acid.[494] This bicyclic isomer was produced previously by treatment of α-camphorene with acetic acid containing sulfuric acid;[537] unfortunately,[494] it was called "iso-α-camphorene." The structural formula of α-camphorene is established definitely, but formulas of the bicyclic and tricyclic isomers are not settled. Some of the possible structures[494] that can be assigned to these isomers are presented in the following group of α-camphorene isomerizations:



1-(2,6,6-Trimethylcyclohex-1-en-1-yl)-3,7,12,16-tetramethyl-18-(2,6,6-trimethylcyclohex-2-en-1-yl)-octadecanonaene-1,3,5,7,9,11,13,15,17 (*i.e.*, pseudo-α-carotene) has been converted into 1,18-bis-(2,6,6-trimethylcyclohex-1-en-1-yl)-3,7,12,16-tetramethyl-octadecanonaene-1,3,5,7,9,11,-13,15,17 (*i.e.*, β-carotene), and vice versa. The processes used are:

chromatographic or differential adsorption on alumina,[210] addition of iodine to benzine solutions,[661] and aging of solutions made up with light petroleum and benzene.[102] These isomerizations involve the shift of only one double bond (in a ring), out of a total of 11 double bonds in the molecule. α-Carotene, which is a geometrical isomer of pseudo-α-carotene [210] and of neo-α-carotene,[211] has been reported to isomerize into neocarotene by treatment with magnesium oxide [210] or alumina.[210, 211] Neocarotene is probably a *structural* isomer with 9 conjugated double bonds.[210] It is converted into neo-α-carotene upon mere crystallization.[211] Neo-α-carotene subjected to adsorption on alumina probably yields β-carotene and neocarotene. These several isomerizations can be considered as interconversions of 5 related deoctahydro-tetraterpenes or carotenoids:

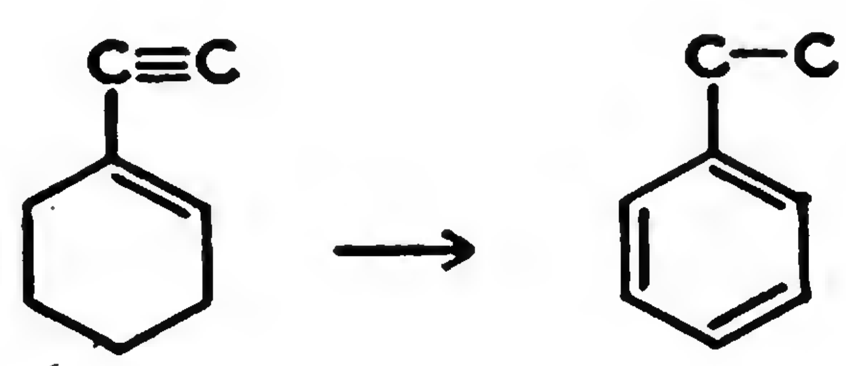




Pseudo-α-Carotene. (This is a second geometrical isomer of α-Carotene)

Pseudo-α-carotene has been found among the oxidation products of β-carotene with dilute potassium permanganate solution, as determined by subsequent chromatographic adsorption on calcium hydroxide.[296, 297] The carotenes are hydrocarbon members of an important and interesting group (carotenoids) of polyene pigments present throughout the plant and animal kingdom.[71aa, 71b, 71c]

1-Ethynylcyclohexene-1, passed with carbon dioxide over platinum-charcoal at 200-205°, was isomerized completely into ethylbenzene:[344]



This remarkable reaction indicates that aromatizations of cyclohexenes into valuable aromatics can be expected to occur by isomerization alone whenever alkynyl groups are present in the molecule. The mechanism involves a transfer of 4 hydrogen atoms from the ring to the side-chain, and a stabilization of the molecule through resonance effects.

Isomerizations of cyclenes with unsaturated side-chains are listed in Table 24, p. 322.

Conclusions

1. Cyclenes with unsaturated side-chains undergo isomerization by: (a) shifts of double bonds present in the ring or side-chain, and (b) cyclization into bicyclic or tricyclic isomers.

2. Catalysts of mild activity, such as alumina, "Floridin," and magnesia, may effect an isomerization by the shift of only one double bond, even though as many as 11 double bonds are present in the molecule.

3. Acids cause cyclization and a shift of side-chain double bonds into the rings newly formed or already present.

4. A cyclohexene with an alkynyl side-chain gives an aromatic in the presence of platinum-charcoal (a useful isomerization).

Cyclodienes with Saturated Side-Chains

Isomerizations

Only a few examples of isomerization are available in the group of cyclodienes (monocyclodiolefins) with saturated side-chains. 1-Methyl-

4-isopropylcyclohexadiene-1,3 (*i.e.*, α-terpinene), treated with phosphoric acid for 200 hours at room temperature, remains unisomerized and can be recovered unchanged.[103] This behavior is expected on account of easy formation from its isomers, the terpenes, and its symmetrical structure (see page 130).

1-Methyl-4-isopropylcyclohexadiene-1,4 (*i.e.*, γ-terpinene) is believed to undergo an isomerization to 1-methyl-4-isopropylcyclohexadiene-1,3 (*i.e.*, α-terpinene) when treated with acidic reagents.[206b] Nine per cent of α-terpinene-maleic anhydride adduct was formed when γ-terpinene and maleic anhydride were heated together[206b] in the customary manner.[206a]

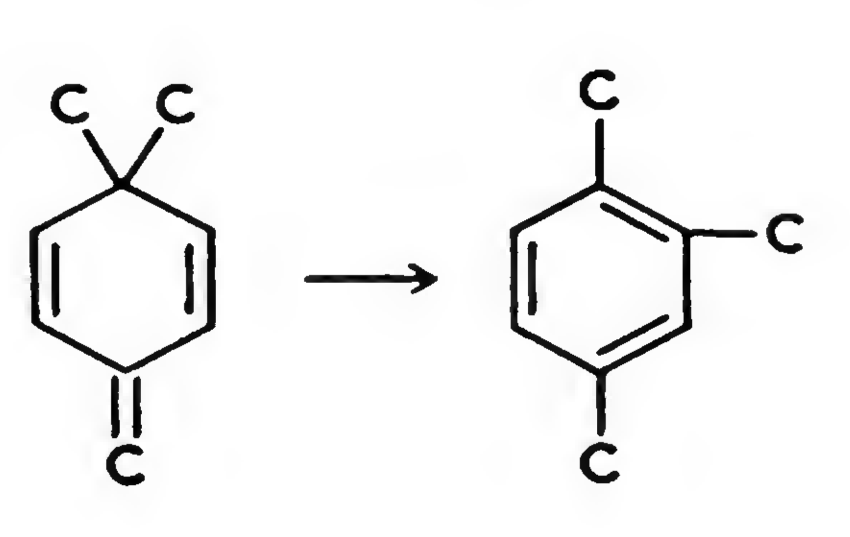
l-1-Methyl-4-isopropylcyclohexadiene-1,5 (*i.e.*, *l*-α-phellandrene) isomerized into α- and γ-terpinenes under the catalytic action of phosphoric acid.[103] This reaction was accompanied by the formation of polymers. When heated for several hours under reflux with alcoholic sulfuric acid, a preparation rich in α-phellandrene gave resins and a volatile fraction containing "terpinene."[617] Mere shaking of *d*-α-phellandrene with alcoholic sulfuric acid for a few minutes also gives "terpinene."[619]

The isomerizations of α-terpinene and α-phellandrene in the presence of catalysts are listed in Table 25, p. 328.

Cyclodienes with Unsaturated Side-Chains

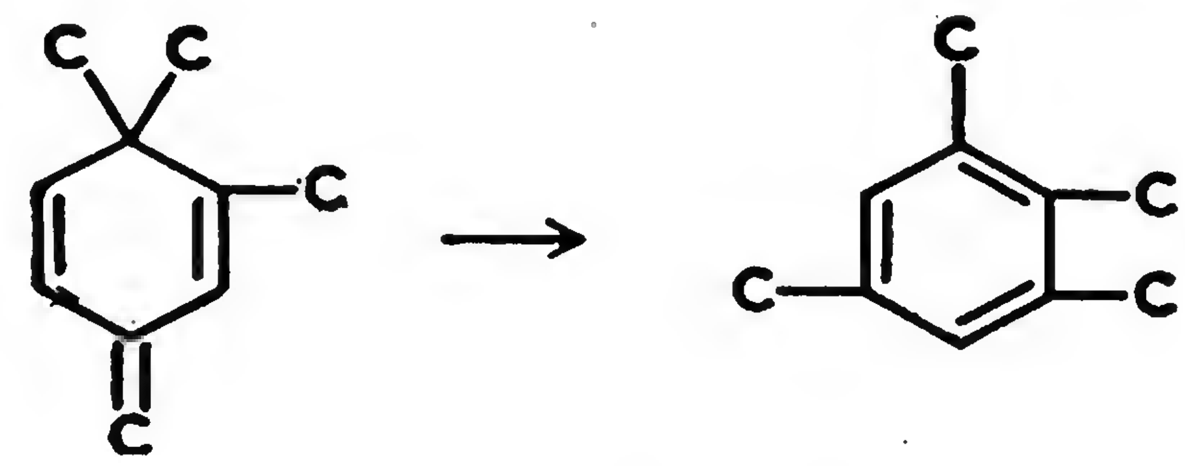
Isomerizations

The cyclodienes containing a six-carbon ring and 3 double bonds per molecule can isomerize irreversibly to a system of 3 conjugated double bonds (aromatics). This has been accomplished by the catalytic action of hydrochloric or sulfuric acid on cyclodiene hydrocarbons of the "semi-benzene" type (acetic acid solutions).[23] 1,1-Dimethyl-4-methylenecyclohexadiene-2,5, the simplest semi-benzene known, isomerized into 1,2,4-trimethylbenzene (pseudocumene), within one hour at 0° in acetic acid solution saturated with hydrogen chloride.[23] The same reaction occurred probably spontaneously when 1,1-dimethyl-4-methylenecyclohexadiene-2,5 was heated alone to about 160° at atmospheric pressure:[22]

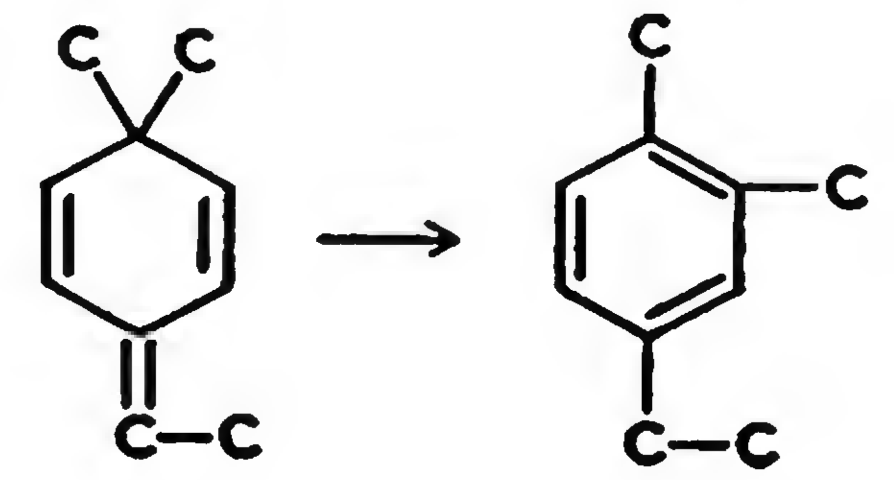


1,1,2-Trimethyl-4-methylenecyclohexadiene-2,5, treated in acetic acid solution with sulfuric acid, probably formed a small amount of 1,2,3,5-

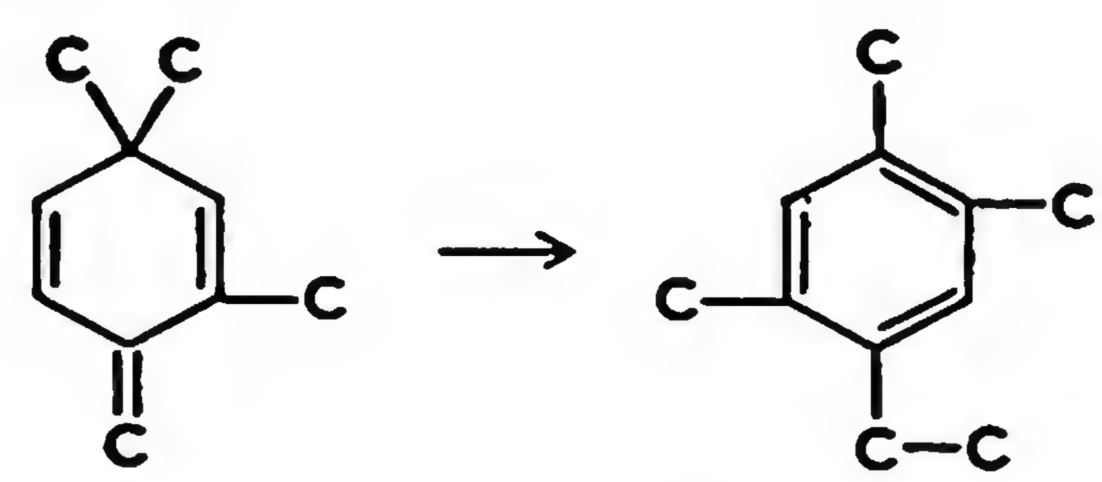
tetramethylbenzene (isodurene), and a large amount of a polymerization product:[23]



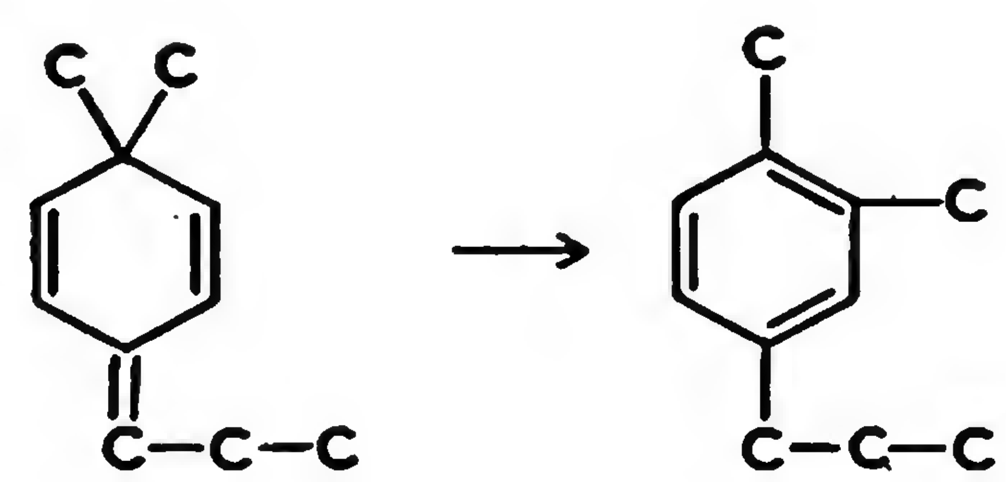
1,1-Dimethyl-4-ethylidenecyclohexadiene-2,5, in acetic acid, formed 1,2-dimethyl-4-ethylbenzene when treated with hydrochloric acid:[23]



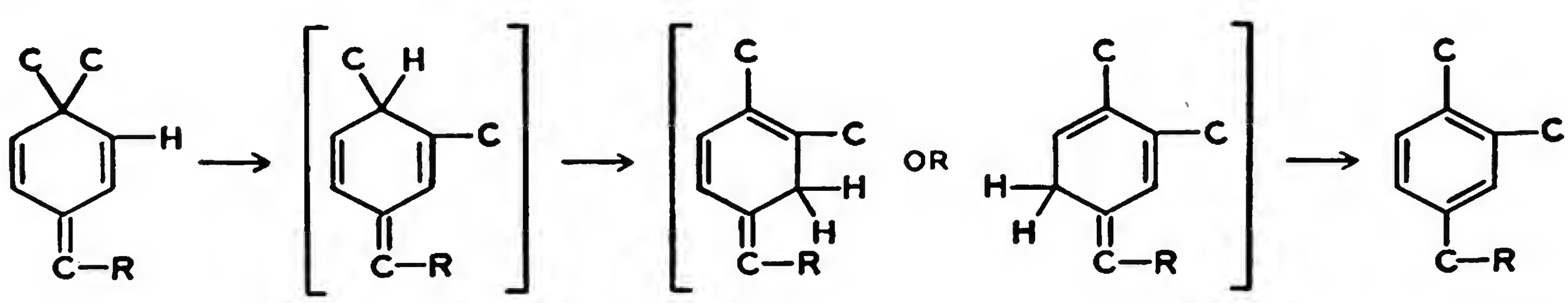
1,1,3-Trimethyl-4-ethylidenecyclohexadiene-2,5 (in acetic acid) gave 1,2,5-trimethyl-4-ethylbenzene (*i.e.*, sym-ethyl-pseudocumene) upon the addition of 70-per cent sulfuric acid.[23] The reaction is exothermic, and the temperature of the mixture changed from 20° to a final 40°:



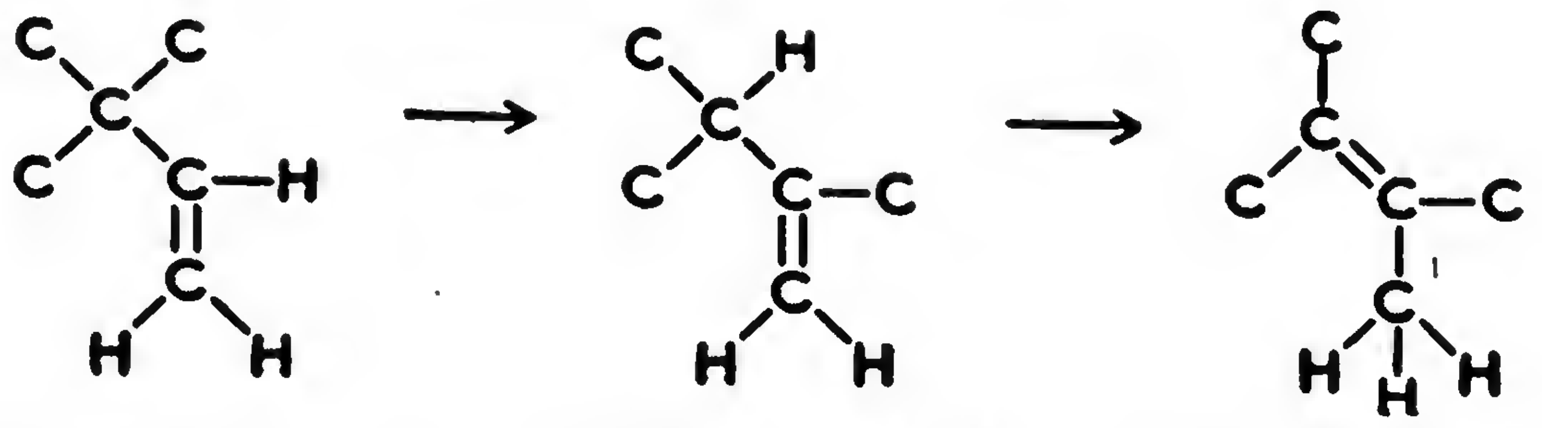
1,1-Dimethyl-4-propylidenecyclohexadiene-2,5, in acetic acid solution containing a little hydrochloric acid, gave 1,2-dimethyl-4-propylbenzene:[23]



The five preceding instances of isomerization are of the following type:

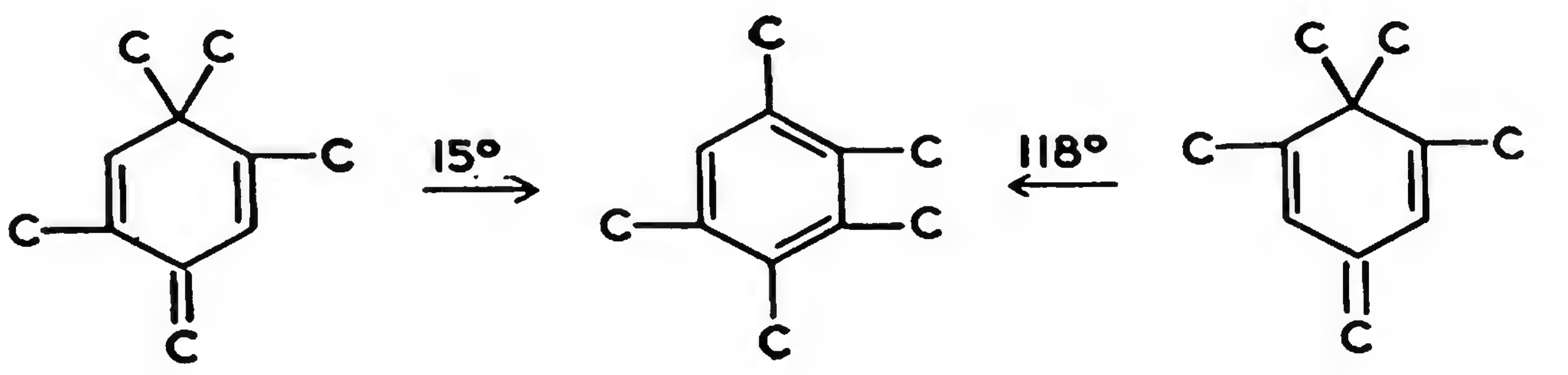


They correspond to the formations of 2,3-dimethylbutene-2 from 3,3-dimethylbutene (via 2,3-dimethylbutene-1) and of α-terpinene from terpinolene:

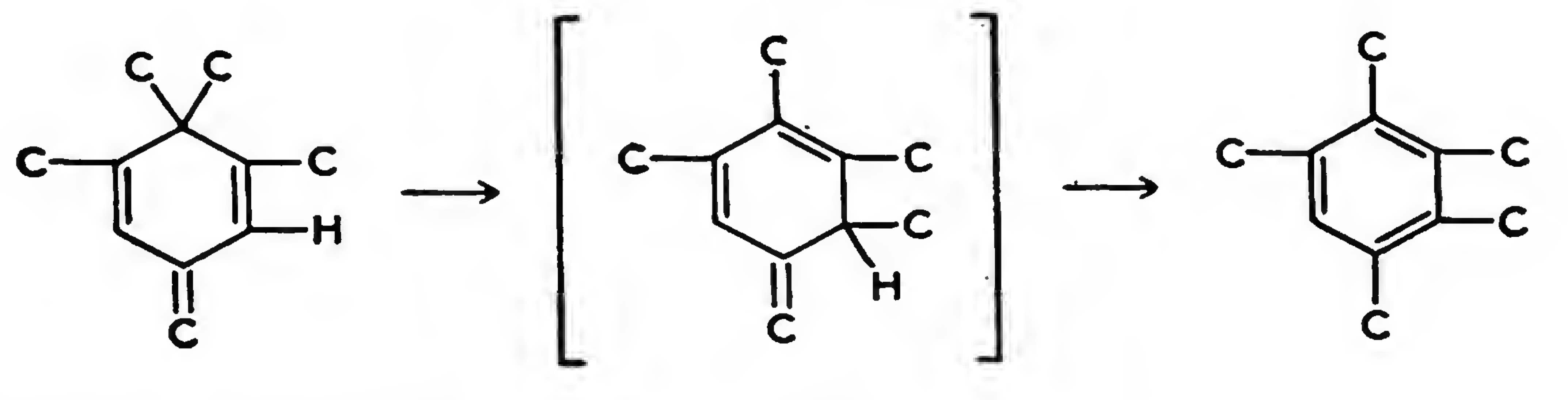


3,3-Dimethylbutene 2,3-Dimethylbutene-1 2,3-Dimethylbutene-2

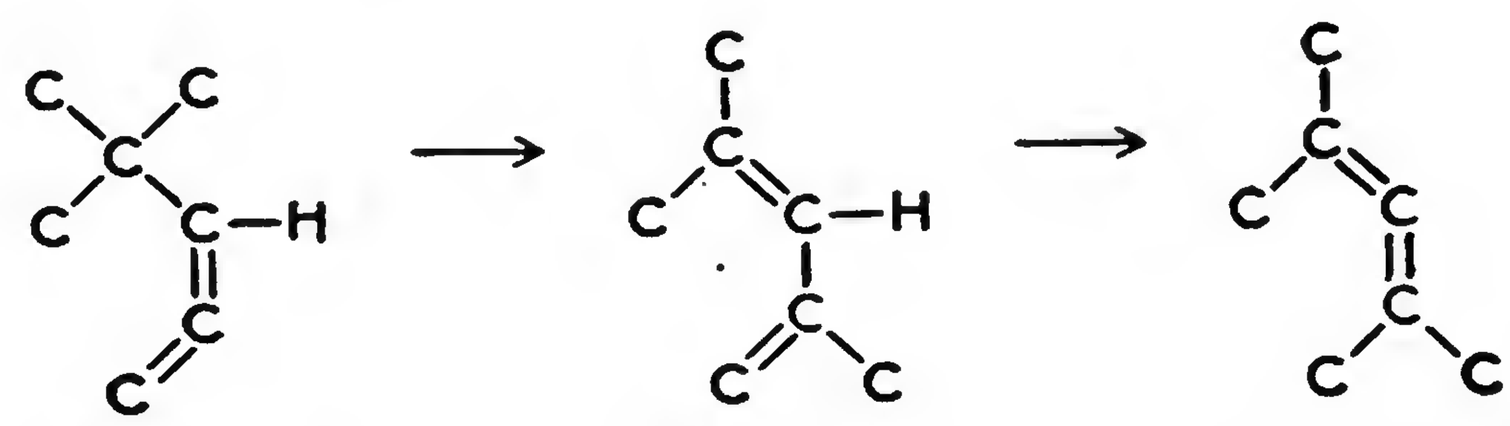
1,1,2,5- and 1,1,2,6-Tetramethyl-4-methylenecyclohexadienes-2,5 (in acetic acid) yielded pentamethylbenzene when treated with hydrochloric and sulfuric acids, respectively.[23] The first hydrocarbon reacted rapidly with development of heat (temperature range, 15° to 30°), whereas the second hydrocarbon required *heating* to the boiling point:



The isomerization of 1,1,2,6-tetramethyl-4-methylenecyclohexadiene-2,5 into pentamethylbenzene is similar to that of 4,4-dimethylpentadiene-1,2 into 2,4-dimethylpentadiene-2,3. The isomerization of 1,1,2,6-tetramethyl-4-methylenecyclohexadiene-2,5 probably involves a preliminary alkyl and unsaturated-bond shift without hydrogen transfer, since the corresponding initial isomerization of 4,4-dimethylpentadiene-1,2 into 2,4-dimethylpentadiene-1,3 occurs without hydrogen transfer:



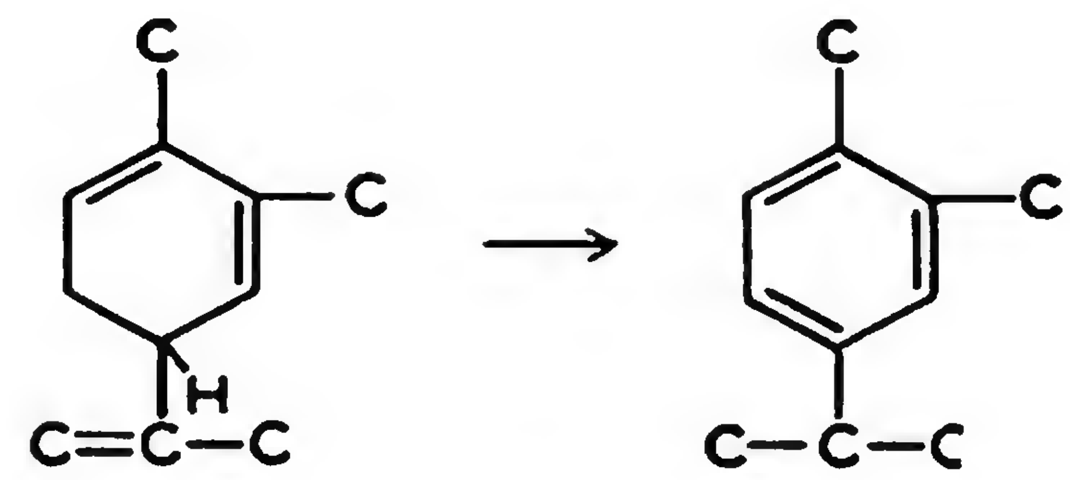
which corresponds to the isomerizations:



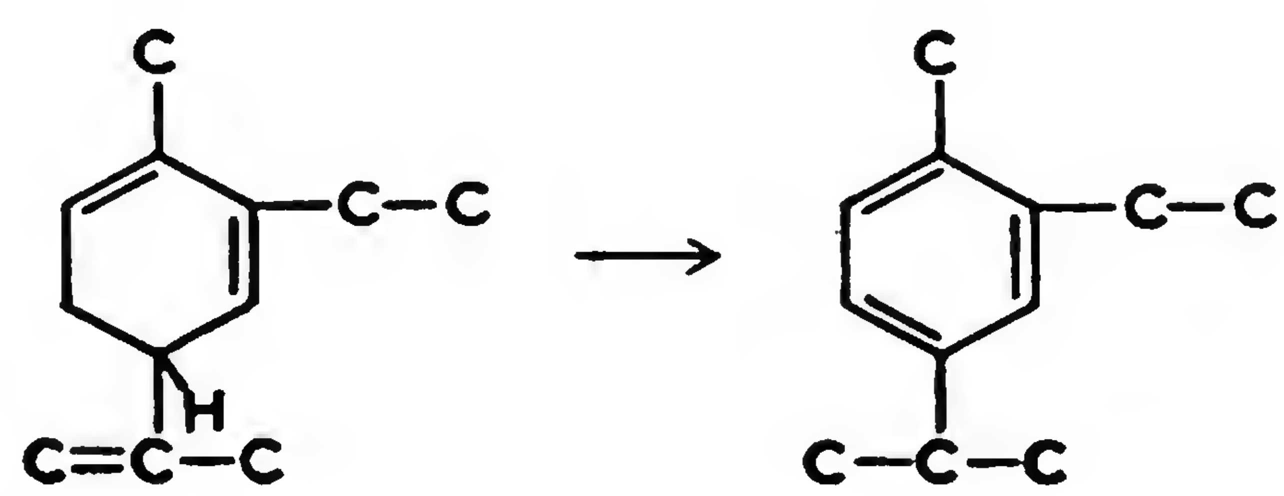
4,4-Dimethylpentadiene-1,2 2,4-Dimethylpentadiene-1,3 2,4-Dimethylpentadiene-2,3

These isomerizations are completed by a prototropic three-carbon, or "terpinolene → α-terpinene," change.

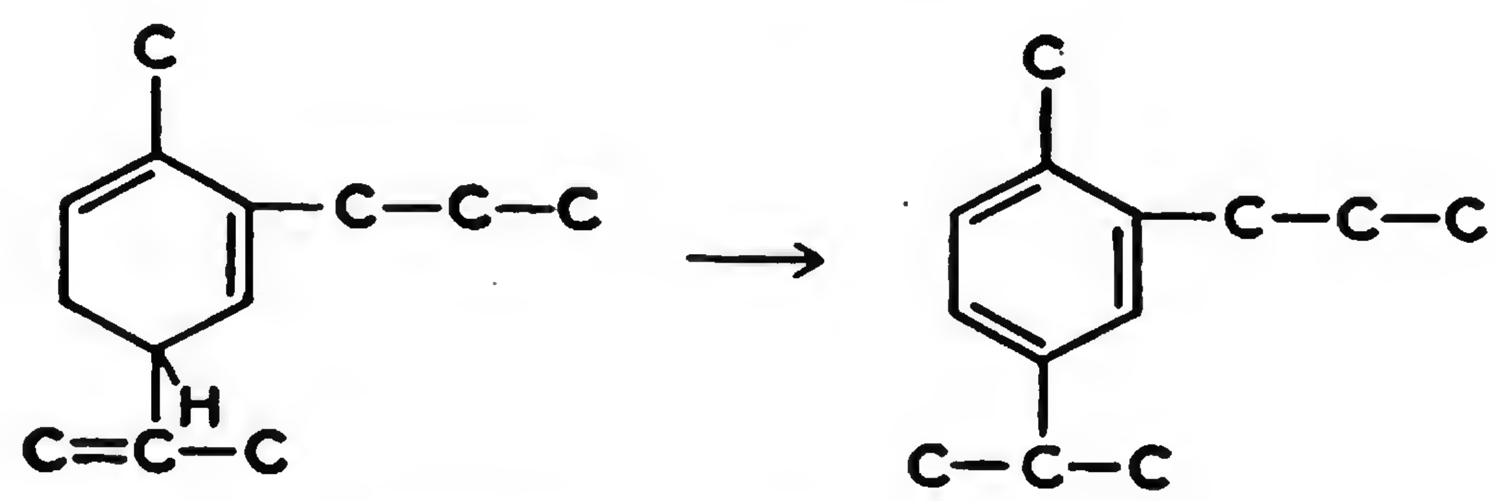
d-1,2-Dimethyl-4-isopropenylcyclohexadiene-2,6 was heated under reflux for 5 hours with 2-per cent hydrogen chloride in acetic acid, forming 70 per cent of 1-2-dimethyl-4-isopropylbenzene:[311]



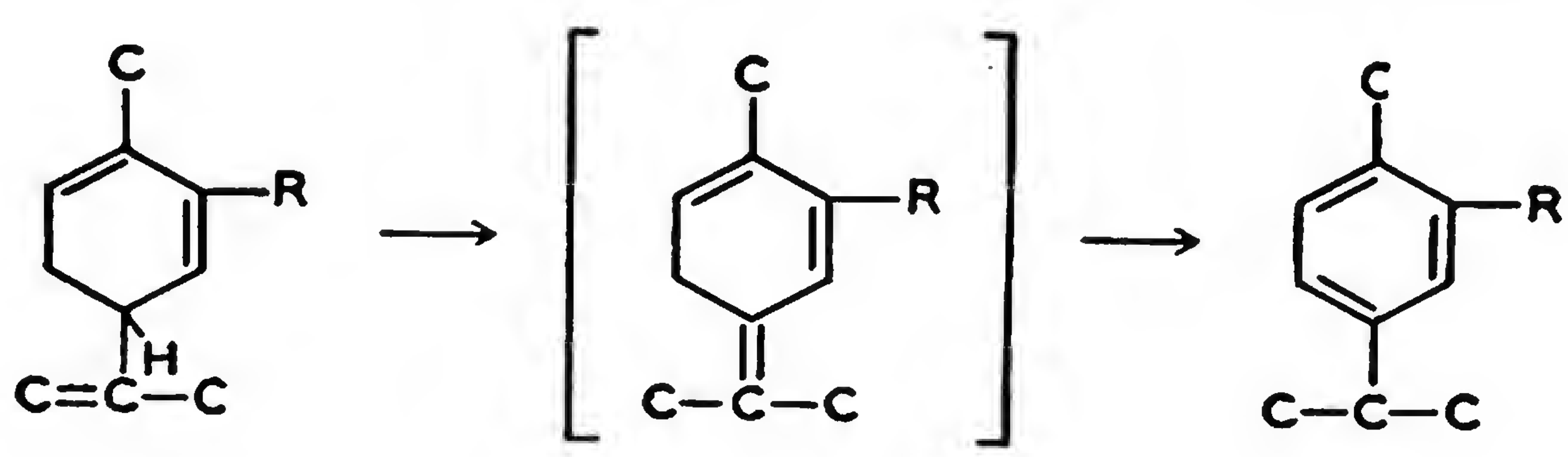
d-1-Methyl-2-ethyl-4-isopropenylcyclohexadiene-2,6, heated under reflux for 5 hours with 2-per cent hydrogen chloride in acetic acid, formed 1-methyl-2-ethyl-4-isopropylbenzene:[311]



d-1-Methyl-2-propyl-4-isopropenylcyclohexadiene-2,6, treated for 4 hours with 3-per cent hydrogen chloride in acetic acid, gave 60 per cent of 1-methyl-2-propyl-4-isopropylbenzene:[310]



The three preceding isomerizations correspond to the stepwise formation of terpinolene and α-terpinene from limonene; they are examples of a simple type of aromatization by hydrogen migration:



l-β-Curcumene is a monocyclic-sesquiterpene mixture containing 1-methyl-4-(1,5-dimethylhex-4-en-1-yl)-cyclohexadiene-1,4 and 1-methyl-4-(1,5-dimethylhex-5-en-1-yl)-cyclohexadiene-1,4.[101] It underwent isomerization to isomers of unknown structure when (a) heated at 380° in an inert atmosphere under pressure, or (b) treated with sodium plus amyl alcohol, or (c) subjected to 10-per cent sulfuric acid for several hours.[459] The last reagent gave a levorotatory bicyclic sesquiterpene.

Isomerizations of cyclodienes with unsaturated side-chains are given in Table 26, p. 328.

Conclusions

1. The conversion of alkenyl-polyalkyl cyclohexadienes-2,6 into poly-

alkyl benzenes (by acids) is one of the simpler forms of isomerization by "aromatization."

2. The isomerization of alkylidene-polyalkyl cyclohexadienes-2,5 into polyalkyl benzenes (by acids) is a less simple aromatization because of an additional step, namely, conversion into intermediary alkylidene-polyalkyl cyclohexadienes-1,5 (or -2,6).

3. The isomerization of 1,1,2,6-tetramethyl-4-methylenecyclohexadiene-2,5 into pentamethylbenzene is an example of a complex aromatization whose mechanism is nevertheless understood.

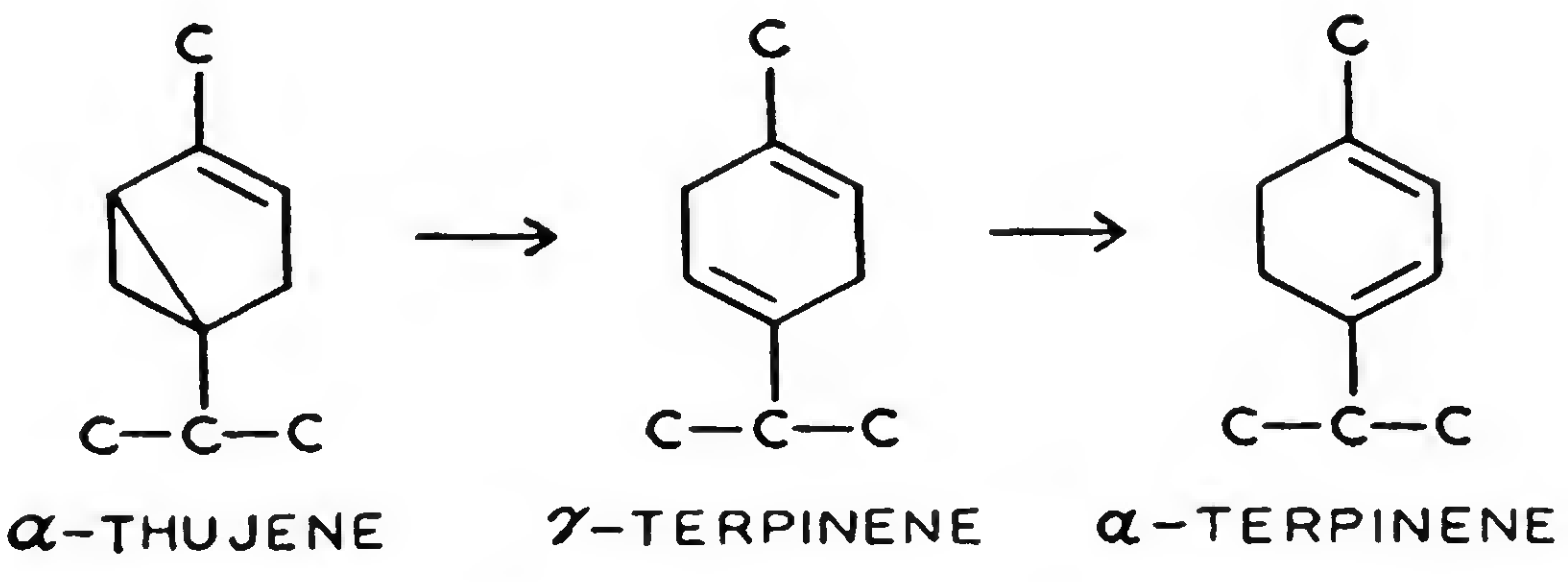
4. β-Curcumene isomerizes by cyclization, which may be highly competitive with aromatization of its two components.

Bicyclenes and Bicyclenes with Saturated Side-Chains

Isomerizations

Several examples of isomerization are available in the group of bicyclenes (*i.e.*, bicycloölefins) with saturated side-chains or without side-chains. *d*-2-Methyl-5-isopropylbicyclo[3.1.0]hexene-2 (*i.e.*, *d*-α-thujene) racemizes very slowly on mere standing.[546] Formation of the *levo* modification is apparently the basis of this "inversion," but a decyclization-isomerization is another possibility.

Decyclization of α-thujene at its weakest point, the incorporated cyclopropane ring, should yield both 1-methyl-4-isopropylcyclohexadiene-1,4 (*i.e.*, γ-terpinene) and 1-methyl-4-isopropylcyclohexadiene-1,5 (which is α-phellandrene) under mild reaction conditions. Partially racemized *d*-α-thujene, when subjected to the rather severe action of alcoholic hydrochloric acid under reflux for 15 minutes, followed by a special treatment of the recovered hydrocarbons (containing also α-terpinene mono- and dihydrochlorides) with maleic anhydride in acetone, yielded 45 per cent of free γ-terpinene and 20 per cent of α-terpinene-maleic anhydride adduct.[206b] A stepwise transformation of α-thujene into γ-terpinene and α-terpinene was postulated:

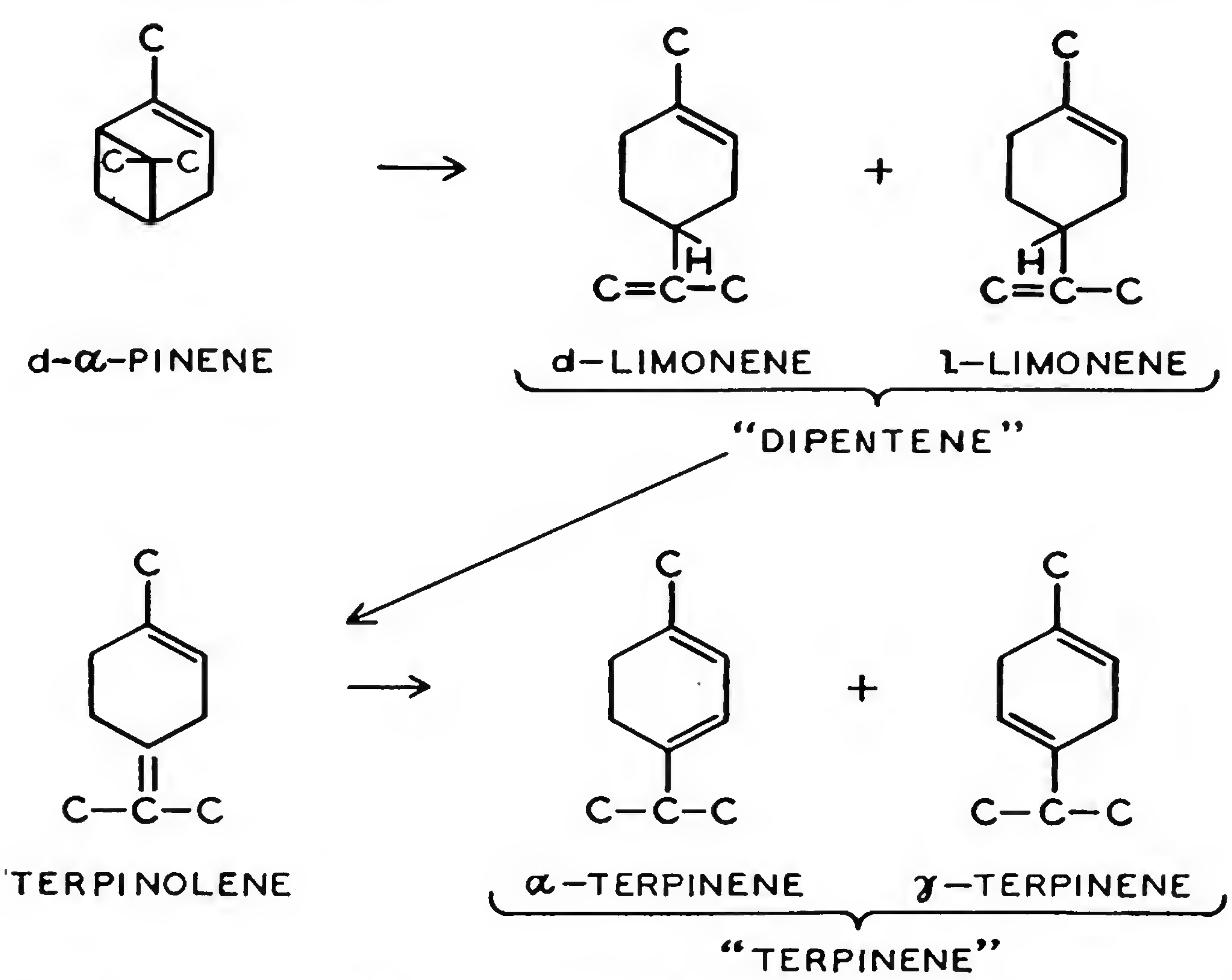


However, 3 per cent of *dl*-α-phellandrene-maleic anhydride adduct and 16 per cent of α-terpinene-maleic anhydride adduct were formed when α-thujene and maleic anhydride were heated together[206b] in the customary manner.[206a] A considerable amount of *p*-cymene was obtained as a by-product. α-Thujene yielded 7 per cent of α-terpinene-quinone

adduct, besides quinhydrone, when heated for 2 hours under reflux with quinone and alcoholic hydrochloric acid.[206b]

2,6,6-Trimethylbicyclo[3.1.1]heptene-2 (*i.e.*, α-pinene) is a terpenic bicyclene that has been studied extensively. Its isomerization proceeds by a breaking and rearrangement of rings with the formation of open-chain, monocyclic, and bicyclic hydrocarbons. An isomerization of α-pinene into β-pinene has not been observed to date,[466, 663] although an analogous shift of the double bond occurs in the formation of camphene.

The isomerization by scission of *one* ring occurs at moderate temperatures. Heating of α-pinene (American turpentine oil) for one hour at 250-270° [615] or for 2 hours at 300° [60, 462] caused isomerization into dipentene and a partial polymerization. This "inversion" of optically active α-pinene by heat "without catalysts" leads always to dipentene [112] and not to *dl*-α-pinene, as has been reported erroneously.[557] Catalysts lower the reaction temperature: active carbon,[377] alumina,[391] thoria,[105] fuller's earth,[610] phosphoric acid,[103, 255, 502] sulfuric acid, [105, 149, 254, 615, 616, 617] and chloroacetic acid [133a] have converted α-pinene into dipentene, terpinene, and terpinolene. Even treatment of *d*-α-pinene (French turpentine oil) with hydrogen (110-120 atm.) in the presence of copper oxide at 240°, or of iron, gives dipentene, rather than hydrogenated products.[272] Arsenic acid is a good catalyst for the formation of "terpinene," since it reacts readily with limonene.[208, 209] The foregoing isomerizations of *d*-α-pinene can be summarized by the following reactions:

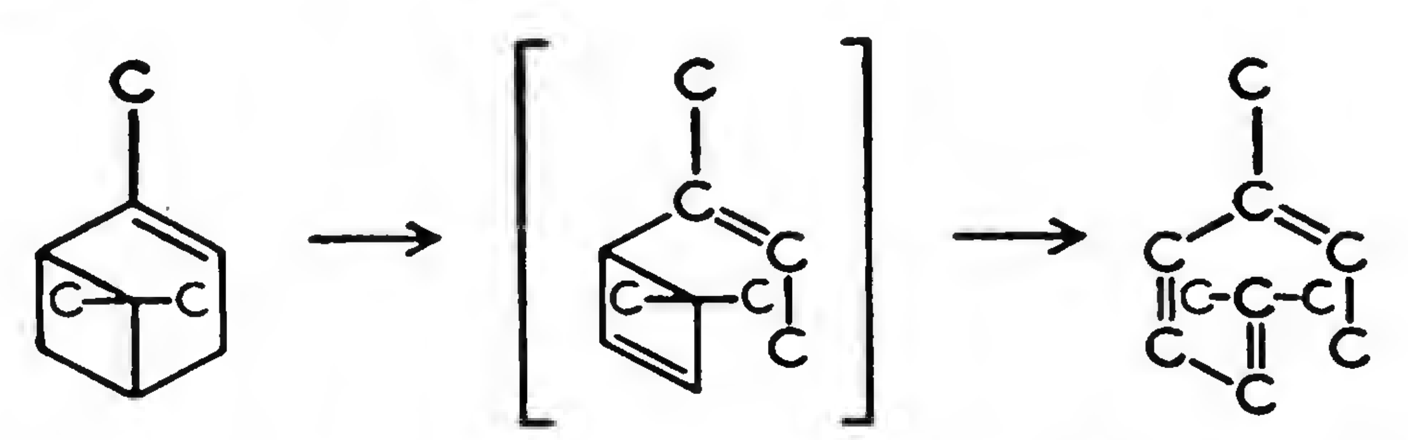


American turpentine oil (essentially α-pinene), heated at 100° for several hours with 25-per cent hydrochloric acid and alcohol, formed a little dipentene, together with a large amount of chlorinated products.[615] A mixture of American turpentine oil, alcohol, and nitric acid (sp. gr. 1.255), when heated slightly, also gave dipentene.[615]

α-Pinene did not isomerize in the presence of 1.0*N* phosphoric acid. A treatment with 3.5*N* acid for 5 hours, however, gave camphene and dipentene, besides ethyl terpinyl ether, terpineol, and $C_{10}H_{16} \cdot H_3PO_4$.[255] The use of 10*N* phosphoric acid resulted in the formation of terpinolene, *p*-cymene, and cineol.[255] The production of dipentene and terpinolene, by heating α-pinene with phosphoric acid at 70-100°, is the subject of recent patents.[541, 542] It has been stated that *l*-α-pinene, heated with acetic acid containing phosphoric acid, gives a considerable amount of *l*-limonene.[448]

The "inversion" of α-pinene by sulfuric acid gives terpinolene (b.p. 185-190°).[616, 617] The heating of American turpentine oil, with sulfuric acid (sp. gr. 1.64) plus alcohol for one day at 100°, gave cymene and a fraction (b.p. 180-190°) containing "terpinene."[615, 616] Dipentene may be also a product of this reaction.[191] Turpentine oil (α-pinene), when treated carefully for 2-3 days with concentrated sulfuric acid, and thereafter steam-distilled, gave a main fraction (b.p. 170-190°) containing "terpinene."[617] As an example of the complexity of the isomerization of turpentine oil (essentially α-pinene), by strong acid, there can be cited the case of the formation of complex mixtures[13, 14, 138, 461, 462, 463, 464, 617] designated at times as "terebene" and as "terpilene." These mixtures have been prepared, for example, by agitating a large volume of rectified turpentine oil (12 liters) with 50-per cent sulfuric acid (800 g.) for one day.[149] The product was found to contain camphene, limonene, dipentene, α-terpinene, γ-terpinene, terpinolene, besides cymene, cineol (2 per cent), and 4 new substances.[149] The yield is only 33 per cent, the remainder is polymers.[149] Russian turpentine oil (a mixture of α- and β-pinenes) has been treated for several days with sulfuric acid (sp. gr. 1.64) and alcohol at 100° in order to prepare γ-terpinene and terpinolene.[669a] The β-pinene component probably is transitionally isomerized to α-pinene, since acids are known to convert β-pinene into α-pinene.

A severe isomerization of α-pinene, with rupture of *both* rings, results in the formation of allo-ocimene, which is an aliphatic isomer. The probable course of this reaction may be the intermediary formation of an unstable cyclobutene:[9]

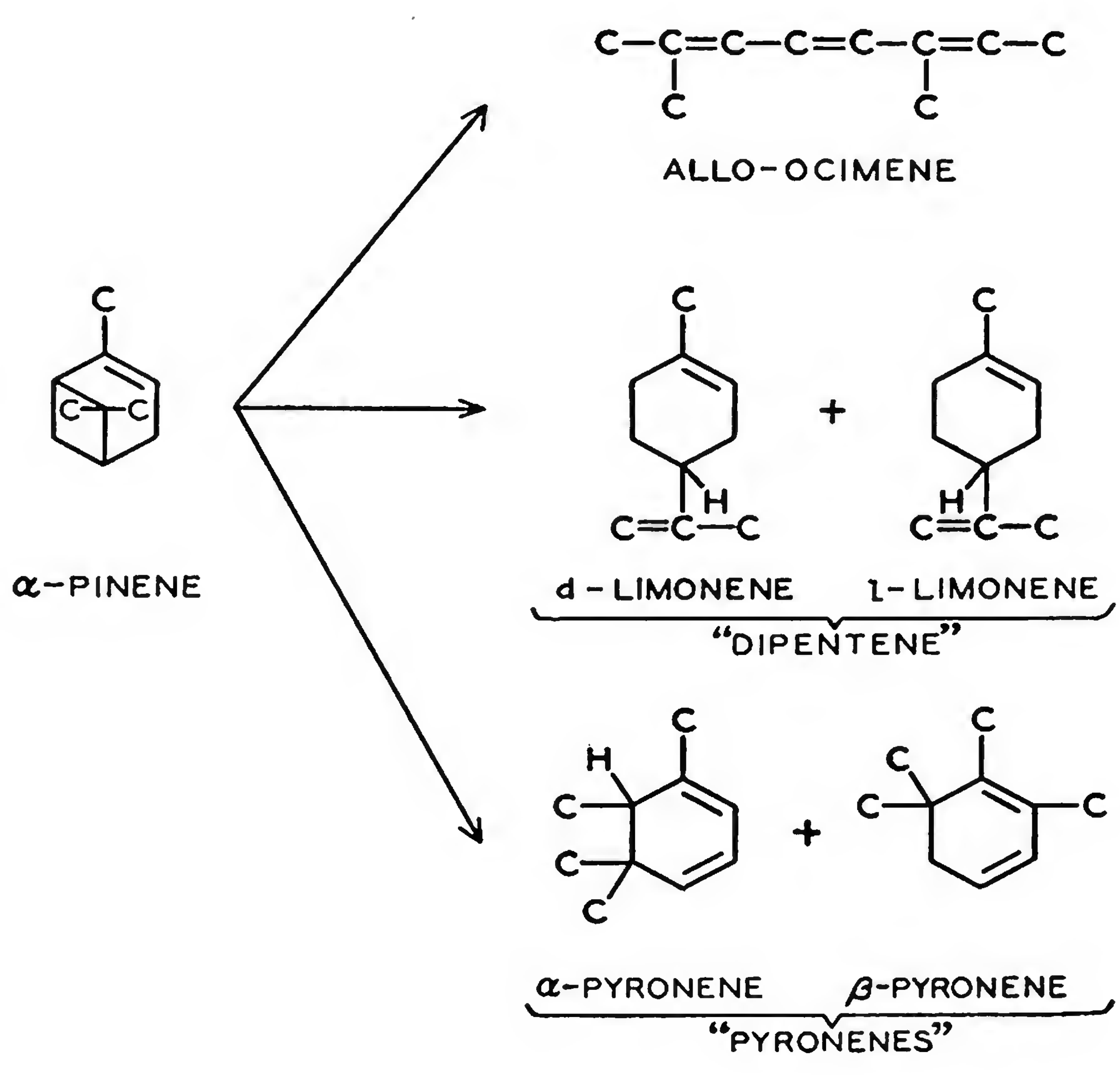


α-Pinene Allo-Ocimene

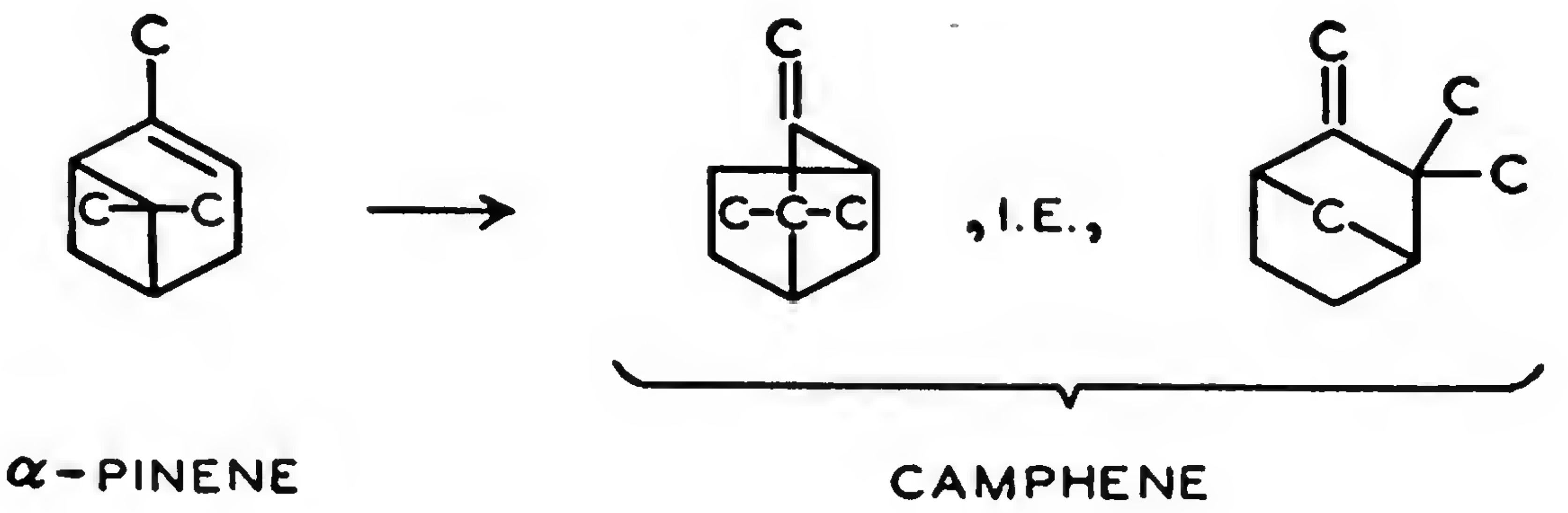
α-Pinene vapors, when passed over a copper chromite catalyst (Adkins') at 375°, or over a cobalt-thorium catalyst (Fischer and Koch's) at 340-400°, gave dipentene and allo-ocimene.[10] Similarly, the passage

of α-pinene vapors over reduced copper at 340-350°, or through a tube filled with chips of "Suprax" glass at approximately 350°, resulted respectively in 26.5 and 24.6 per cent of allo-ocimene.[8, 11] Even ordinary soft glass is effective, yielding 26 per cent of allo-ocimene.[8] These yields were reduced to 17 per cent at 380-390°.[8] This seems to indicate that temperature, time of contact, and heat-transfer coefficients are important factors in this isomerization, rather than the catalyst type. The conduction of *d*-α-pinene, as vapor in nitrogen through a "Pyrex" glass tube heated at 370-375° gave a product containing 6, 6, 40, and 42 per cent of α-pyronene, β-pyronene, allo-ocimene, and dipentene, respectively.[217a] The idea has been advanced [8] that allo-ocimene is a very common product in the isomerization of α-pinene. However, it has probably been missed by previous investigators because of the application of too high temperatures (600-700°),[496] or by mistaking allo-ocimene for a polymerization product.[390]

Passage of α-pinene over copper gauze at 300-350° yielded allo-ocimene, dipentene, and about 50 per cent of α- and β-pyronenes.[144] The yield of allo-ocimene is 30 per cent at 340°.[148] *dl*-α-Pinene, when treated similarly at 350°, gave *dl*-α- and β-pyronenes.[145] Recent work [146] indicates that β-pyronene possesses the structure of 1,2,6,6-tetramethylcyclohexadiene-1,3, possibly because of a shifting of both double bonds in α-pyronene. The earlier assignment [144] of 1,5,5-trimethyl-6-methylenecyclohexene-1 to β-pyronene is now reserved for cyclomyrcene. The formation of dipentene and α-pyronene involves ring scission and the migration of hydrogen (from one of 3 carbon atoms, thereby forming a double bond):



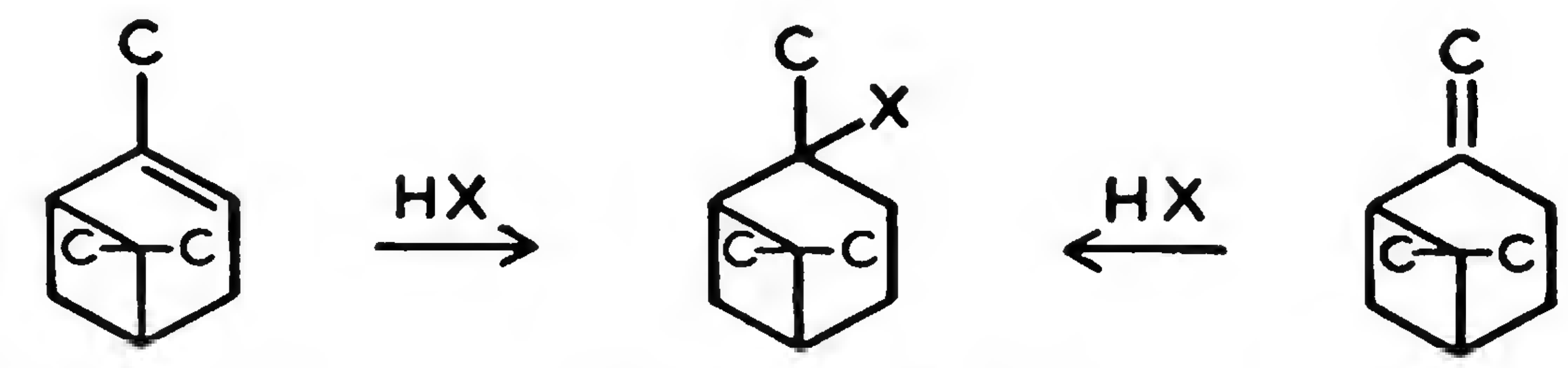
Isomerization of α-pinene by a decyclization occurring at other places in the molecule has been reported. The possibility of such a change is indicated by the conversion of α-pinene into camphene via acids or acidic catalysts:



The isomerization of α-pinene into camphene occurs in the presence of active carbon,[202, 377] red phosphorus,[91, 383] alumina,[91, 383] bauxite,[586] silica,[91, 383, 505] kieselguhr,[91, 383] thoria,[105] aluminum phosphate,[91, 383] calcium phosphate,[91, 383] kaolin,[91, 383, 586] clays,[91, 236, 327, 349a, 383, 586] fuller's earth,[91, 235, 383] acid-treated permutite,[505] various acid phosphates,[508, 514, 601a] highly acidic molybdates, tungstates, or vanadates,[504, 504a, 510] acid phosphotungstates,[514] $CoSO_4 \cdot H_2O$,[503, 513] $FeSO_4 \cdot H_2O$,[503, 513] $MgSO_4 \cdot H_2O$,[459a, 503, 509, 513] $NaHSO_4$,[508] $NiSO_4 \cdot H_2O$,[503, 509, 513] $ZnSO_4 \cdot H_2O$,[503, 513] antimonic acid,[502, 511a, 512, 514, 601a] meta-boric acid,[502, 508] ortho-boric acid,[514] molybdic acid,[502, 514] arsenomolybdic acid,[514] phosphomolybdic acid,[502, 514, 601a] silicic acid,[502, 508, 514] phosphostannic acid,[511a, 514] titanic acid,[502, 508, 514, 601a] tungstic acid,[502, 514, 601a] borotungstic acids,[514] phosphotungstic acid,[502, 514,] silicotungstic acids,[514] vanadic acid,[502, 508, 514, 601a] silicovanadic acid,[514] alcoholic hydrochloric acid,[256] phosphoric acid,[502] alcoholic phosphoric acid,[255] borophosphoric acid,[511, 511a, 514] sulfuric acid,[149, 462, 464] sulfonic acids,[508] formic acid,[460] acetic acid,[35, 36, 75, 662] boracetic acid,[514] chloracetic acid,[133a] oxalic acid,[133a, 508] aluminoxalic acid,[514] chromoxalic acid,[502, 514] benzoic acid,[76] salicyclic acid,[133a] *o*-benzoylbenzoic acid,[133a] phthalic acid,[508] acetic anhydride with boric anhydride,[268, 269] acetic anhydride with ortho-boric acid,[268] colophony,[439] phenol,[322] picric acid,[133, 322] and numerous substituted phenols.[322] These catalysts represent a *whole range of acidities* and yields of camphene up to 85 per cent! The suitability of fuller's earth in the formation of camphene from α-pinene has been questioned.[610]

The formation of camphene from α-pinene and acids is considered to be an example of the "delayed isomerization" and "right-shift" proposed for conversions of β-pinene into camphene. It involves a double Wagner-rearrangement: that of α-pinene into bornyl esters[534, 614] and that of isobornyl esters into isocamphanyl esters.[369, 370] With hydrogen chloride, the logical first step is formation at −60°[370] of the exceedingly unstable true pinene-hydrochloride.[17] The transformation of α-pinene into camphene via acids and acidic catalysts appears to proceed in the

same 5 steps as proposed for the conversion of β-pinene into camphene, since the initial steps give identical nopinyl esters:



α-Pinene   Nopinyl Ester (Unstable)   β-Pinene

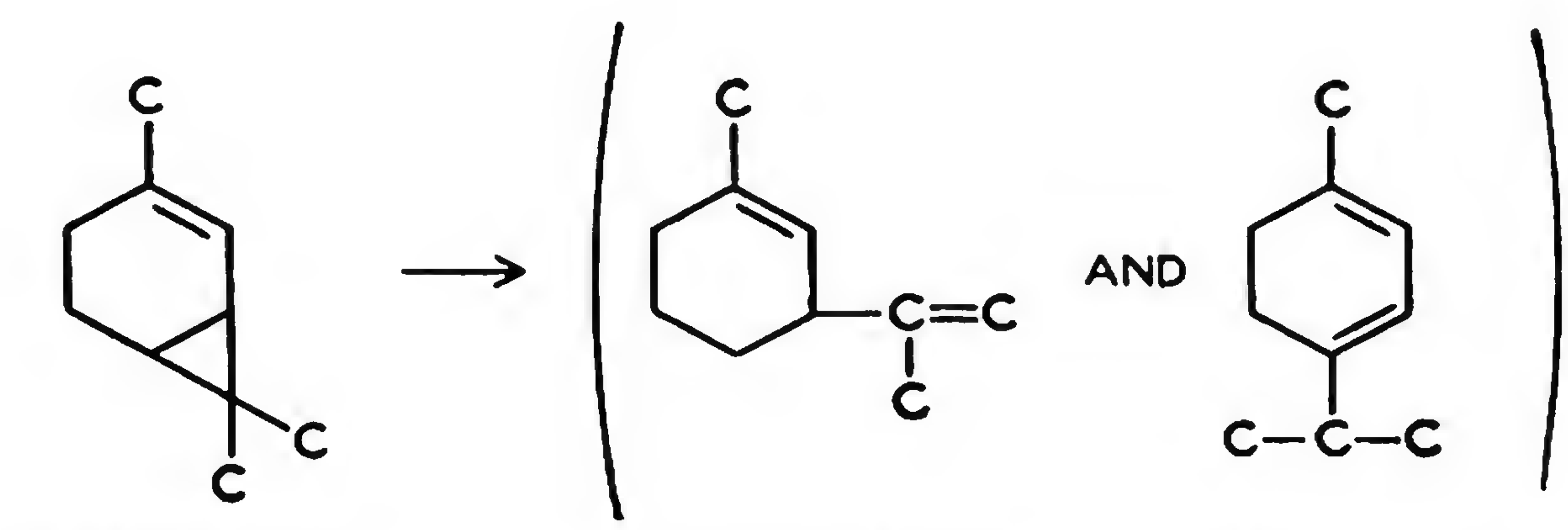
A considerable amount of work has been carried out on the action of *organic* acids on α-pinene. Unfortunately, considerable confusion exists in the literature as to the structures of the usual "hydration" products [77] and the modes of their formation.[36, 322] *d*-α-Pinene, when treated for over two months with formic acid, gave *d*-camphene, *d*-limonene, dipentene, α-terpinene and terpinolene, as isomers, along with recovered *d*-α-pinene, formic acid, *d*-diterpilene, bornyl formate, *d*-4-terpinenyl formate, and *d*-α-terpinyl formate.[460] The treatment of *l*-α-pinene with formic acid gives *l*-limonene.[78, 328] *d*-α-Pinene, when heated at 100° with acetic acid, formed *d*-limonene, *d*-bornyl acetate, *l*-bornyl acetate, and *d*-α-terpinyl acetate.[328] *l*-α-Pinene, treated with acetic acid, gave various proportions of *l*-limonene and *l*-camphene, depending probably on whether the acid used was or was not heated and anhydrous.[35, 36, 75, 662] Other products formed at the same time are *l*-α-terpinyl acetate,[35, 36, 74, 75, 78, 171] (*Ld*)-fenchyl* acetate,[35, 36, 74, 75] *l*-bornyl acetate,[35, 36, 74, 75, 662] isobornyl acetate,[35, 36] and terpin hydrate.[78] *d*-Limonene was found in a free state among the products of esterification of *d*-α-pinene by means of acetic acid containing acetic anhydride and Japanese acid clay.[327a] *l*-α-Pinene, when heated with benzoic acid, formed *l*-camphene, *l*-limonene, *l*-bornyl benzoate, (*Ld*)-fenchyl benzoate, and colophony.[76] The action of phenol and its various substitution products (*o*-cresol, resorcinol, methyl salicylate, *p*-nitrophenol, *p*-nitro-*m*-cresol, *m*-dinitrophenol, dinitro-*o*-cresol, 2,6-dinitro-*p*-cresol, picric acid, 2,4,5-trinitro-*m*-cresol, trinitrothymol, tribromophenol, and trichlorophenol) upon heated *l*-α-pinene gives *l*-camphene and, in some cases, also dipentene, diterpene, a bornyl phenolate, and a trace of water.[322]

l-α-Pinene, when treated with acetic and boric anhydrides at 90-95°, formed *l*-camphene and dipentene, together with bornyl, isobornyl and fenchyl acetates.[268] α-Pinene, heated at 110-120° for 15-18 hours with acetic acid, acetic anhydride, plus boric anhydride, yielded camphene, dipentene, α-terpinene, terpinolene, along with *p*-cymene, bornyl acetate, isobornyl acetate, and possibly also α- and β-fenchyl acetates.[269] *l*-α-Pinene, when heated with acetic anhydride containing ortho-boric

* The symbol *Ld* describes both the actual optical rotation (*d*) and the starting point for a synthesis from fenchone (*l*-form), according to Wallach.[620a]

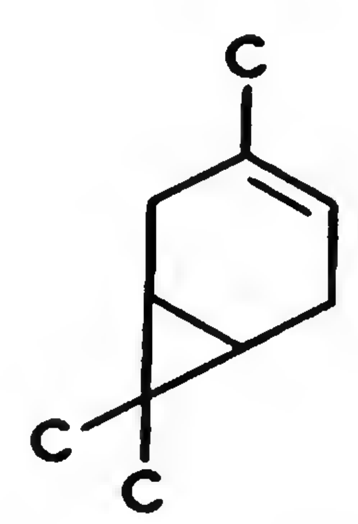
acid gave *l*-camphene, dipentene, cymene, α-fenchyl acetate, β-fenchyl acetate, bornyl acetate, isobornyl acetate, and possibly α-terpinyl acetate and the acetate of some diterpene.[268]

d-3,7,7-Trimethylbicyclo[4.1.0]heptene-2 (*i.e.*, *d*-Δ^4-carene), heated at 280° for 4 hours, gave sylvestrene and α-terpinene.[538] Treated with boiling acetic acid, it formed α-terpinene: [538]



d-Δ^4-Carene Sylvestrene α-Terpinene

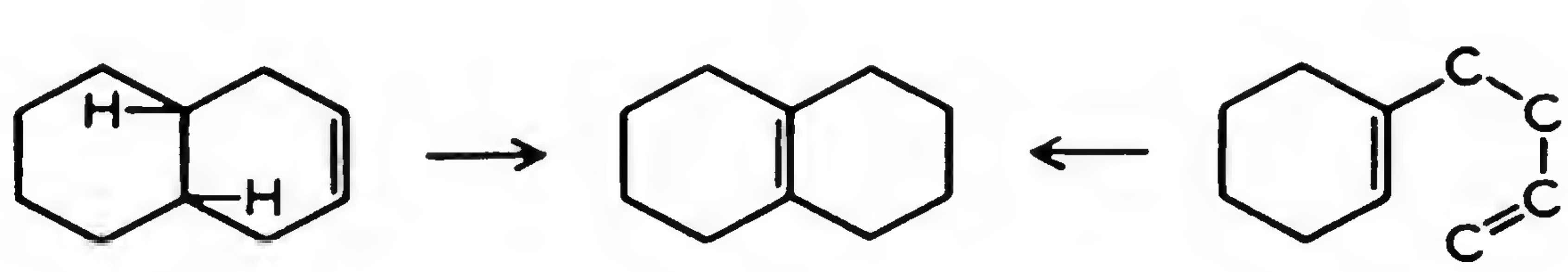
d-3,7,7-Trimethylbicyclo[4.1.0]heptene-3 (*i.e.*, *d*-Δ^3-carene) "passed unchanged" through a "Suprax" glass tube at 400°.[12]



[Unisomerized to date]

d-Δ^3-Carene

The isomerization of 1,6-*trans*-bicyclo[4.4.0]decene-3 (*i.e.*, *trans*-1,2,-3,4,4a,5,8,8a-octahydronaphthalene or *trans*-Δ^2-octalin) into bicyclo-[4.4.0]decene-1[6] (*i.e.*, 1,2,3,4,5,6,7,8-octahydronaphthalene or $\Delta^{9,10}$-octalin), which occurs upon heating under reflux with phosphorus pentoxide for 3 hours at 140°,[353] is of interest in connection with the cyclization of 1-(3-butenyl)cyclohexene-1. This cyclization involves either the intermediary formation of 1,2,3,4,4a,5,6,8a-octahydronaphthalene or the direct formation of 1,2,3,4,5,6,7,8-octahydronaphthalene. The isomerization of *trans*-1,2,3,4,4a,5,8,8a-octahydronaphthalene into 1,2,3,4,5,6,7,8-octahydronaphthalene probably involves the intermediary formations of 1,2,3,4,4a,5,6,8a-octahydronaphthalene and 1-(3-butenyl)cyclohexene-1, rather than that of 1,2,3,4,4a,5,6,7-octahydronaphthalene. The last hydrocarbon is a strained form, according to Bredt's rule,[89] since it has a double bond adjacent to the juncture of 2 fused rings. Under Anthracenes (*supra*), it will be seen that the 3-butenyl group probably enters readily into "alkylation-dealkylation" isomerizations:



The isomerizations of bicyclenes and bicyclenes with saturated side-chains are listed in Table 27, page 330.

Conclusions

The complicated isomerizations of the bicyclenes can be summarized only for the few members investigated to date. Even so, several theoretical possibilities remain to be investigated in the observed examples, such as the relative stability of various atomic and valence bridges.

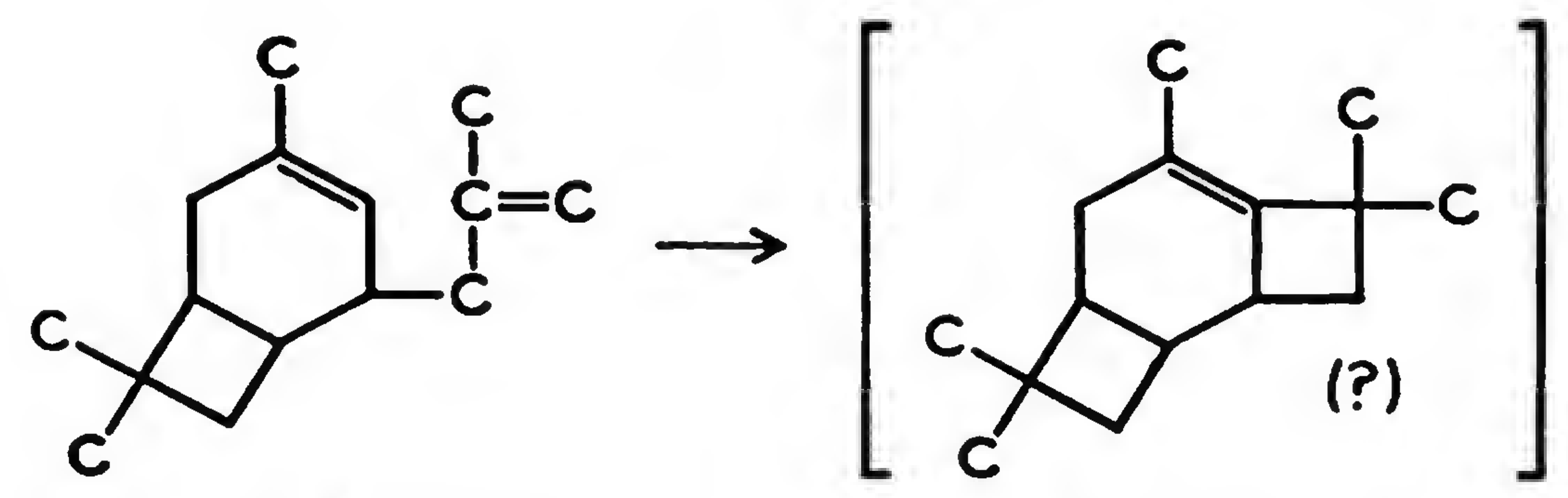
1. The shift of the double bond observed in the case of *trans*-1,2,3,-4,4a,5,8,8a-octahydronaphthalene does not have a counterpart in the numerous isomerizations shown by α-pinene. The double bond of α-pinene apparently stays intact in all paths except that leading to camphene!

2. The complexity of the transformation of α-pinene into camphene is shown by its numerous steps in the presence of acidic catalysts. In such cases where the intermediary salts cannot form (as with heat or certain catalysts), it is suggested that similar steps are operative. Analogous active forms of the molecule (bicyclo-diyls without a negative ion) are suggested as being responsible for the isomerization.

Bicyclenes with Unsaturated Side-Chains

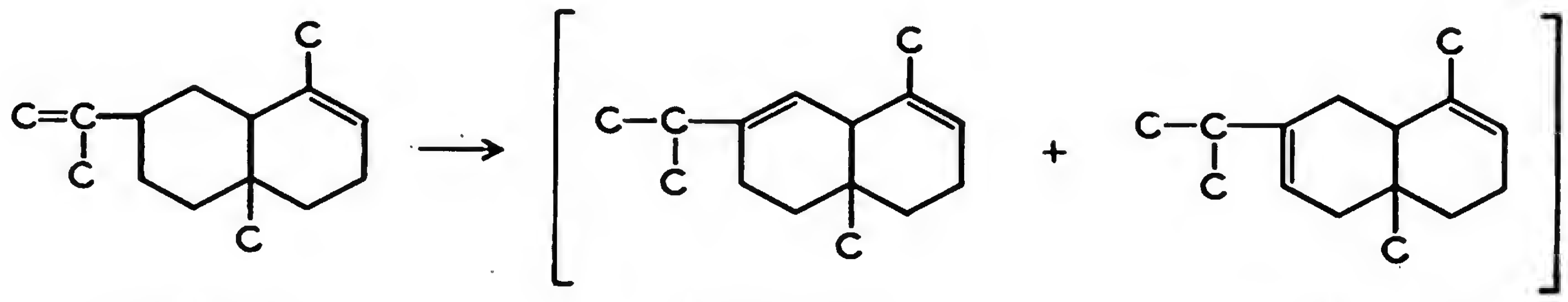
Isomerizations

Ordinary "caryophyllene," which is a mixture of two bicyclic sesquiterpenes from clove oil, is isomerized by treatment with mixed acetic and sulfuric acids, according to the Wallach-Walker [633] and Bertram-Walbaum [65] method of esterification. An early observation [633] states that ordinary "caryophyllene," when heated for 12 hours with acetic acid plus dilute sulfuric acid, gives caryophyllene hydrate ($C_{15}H_{25}OH$, m.p. 96°, hence β-iso-caryophyllene alcohol [488]), which can be dehydrated by phosphorus pentoxide to "clovene" (b.p. 261-263°). The latter should be taken as the higher-boiling component of 2 tricyclic caryophyllenes, which comprise the usual product.[137, 488] Other observations [136, 137] indicate that the treatment with mixed acetic and sulfuric acids gives simultaneously "isocaryophyllene alcohol" (caryophyllene hydrate), clovene (b.p. 261-263°), and the lower-boiling component of the tricyclic sesquiterpene.[136] β-Caryophyllene (bicyclic), when heated under reflux with formic acid for several days, gave "clovene," the formate of a tricyclic alcohol (probably β-iso-caryophyllene formate), and unchanged caryophyllene.[469] Treatment of "caryophyllene" (b.p. 123-124° at 16 mm. Hg) alternately with ethereal sulfuric acid and sodium hydroxide solution formed clovene, α-iso-caryophyllene alcohol (m.p. 116°), and β-iso-caryophyllene alcohol.[488] The cyclization of caryophyllene into clovene can be formulated tentatively, on the basis of a structure [483] proposed for "caryophyllene," as follows:



"Caryophyllene" Clovene

d-α-Selinene was converted readily by alcoholic sulfuric acid into a dextrorotatory product, probably δ- and ϵ-selinenes:[492]



α-Selinene δ-Selinene ϵ-Selinene

l-Sclarene, a bicyclic diterpene obtainable by dehydration of the naturally occurring sclareol, isomerized incompletely to a tricyclic, via cyclization, when heated at 120° for 4 hours with formic acid.[489] Sclarene is considered to be a bicyclene at this point for the purpose of classification, since its structure is unknown.[487]

The experimental data on isomerizations of the bicyclenes with unsaturated side-chains are given in Table 28, p. 352.

Conclusions

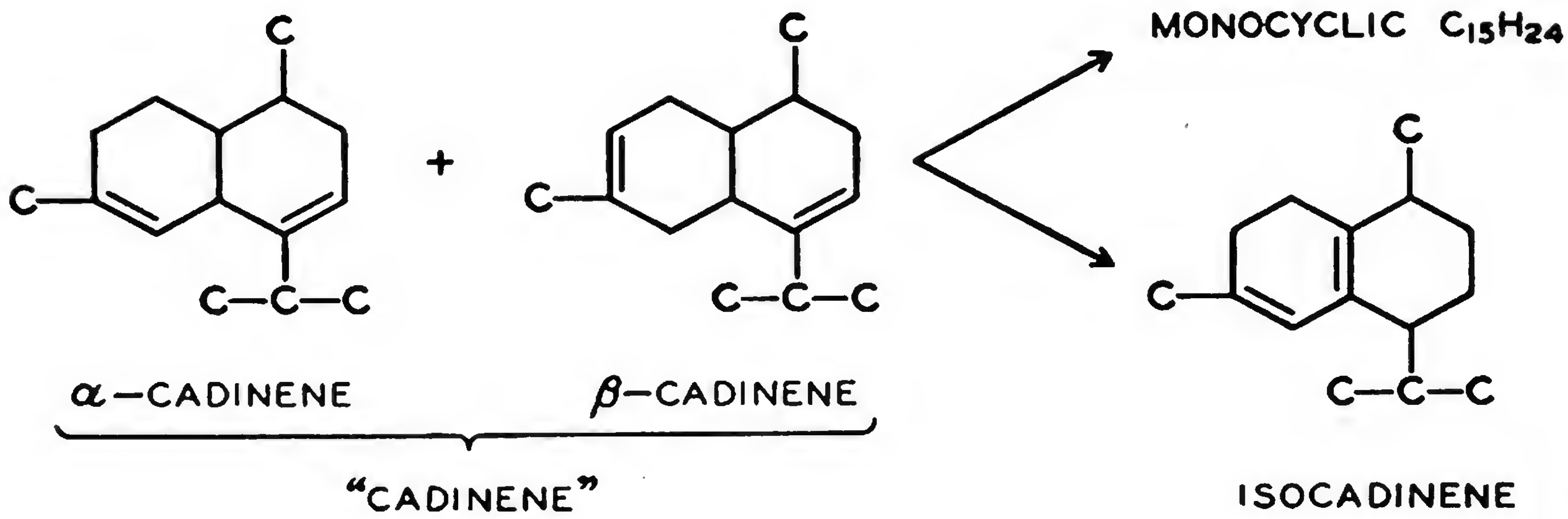
1. The bicyclenes with unsaturated side-chains undergo an isomerization into bicyclodienes or tricyclenes.

2. These products are those expected on the basis of isomerization with acidic catalysts, namely, isomers formed by the shift of double bonds into rings, and/or by cyclization.

Bicyclodienes with Saturated Side-Chains

Isomerizations

The group of bicyclodienes (bicyclodiolefins) has not been studied extensively. l-Cadinene (regenerated) changed partly into a levorotatory monocyclic sesquiterpene when heated at 330° in a bomb tube.[536] Cadinene, heated under reflux for 36 hours with 57-per cent sulfuric acid, gave an isomer of increased boiling point and greater density,[493] thereby confirming an earlier observation that l-cadinene is isomerized when heated for a long time with dilute sulfuric acid.[633] l-Cadinene (regenerated) gave isocadinene when heated at 100° for 8 hours with acetic acid plus sulfuric acid (Bertram-Walbaum method) or heated at 230-235° for 24 hours with acetic acid in a bomb tube.[246]

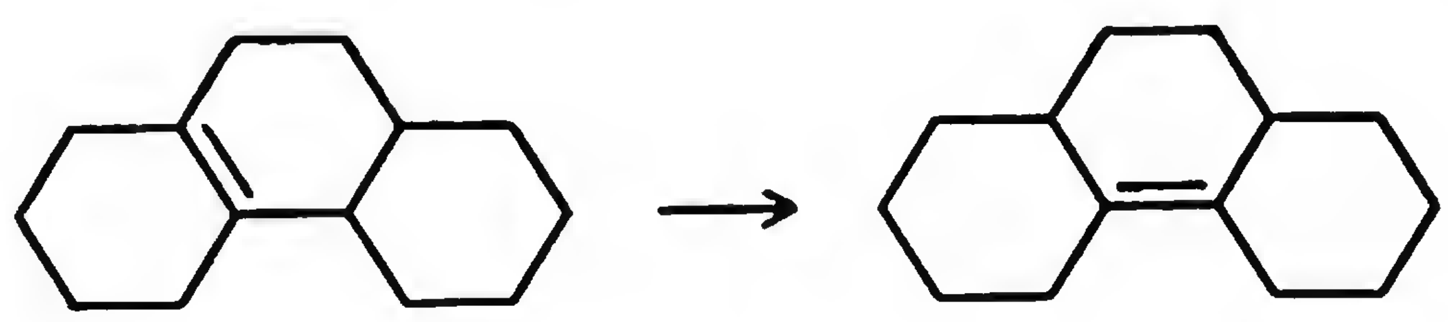


The experimental data are given in Table 29, p. 352.

Tricyclenes and Tricyclenes with Saturated Side-Chains

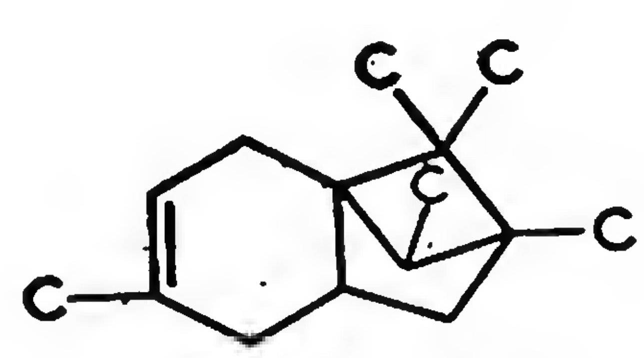
Isomerizations

Mere distillation (10-26 mm. Hg) of $\Delta^{11,12}$-dodecahydrophenanthrene gave the more symmetrical $\Delta^{12,13}$-dodecahydrophenanthrene:[150]



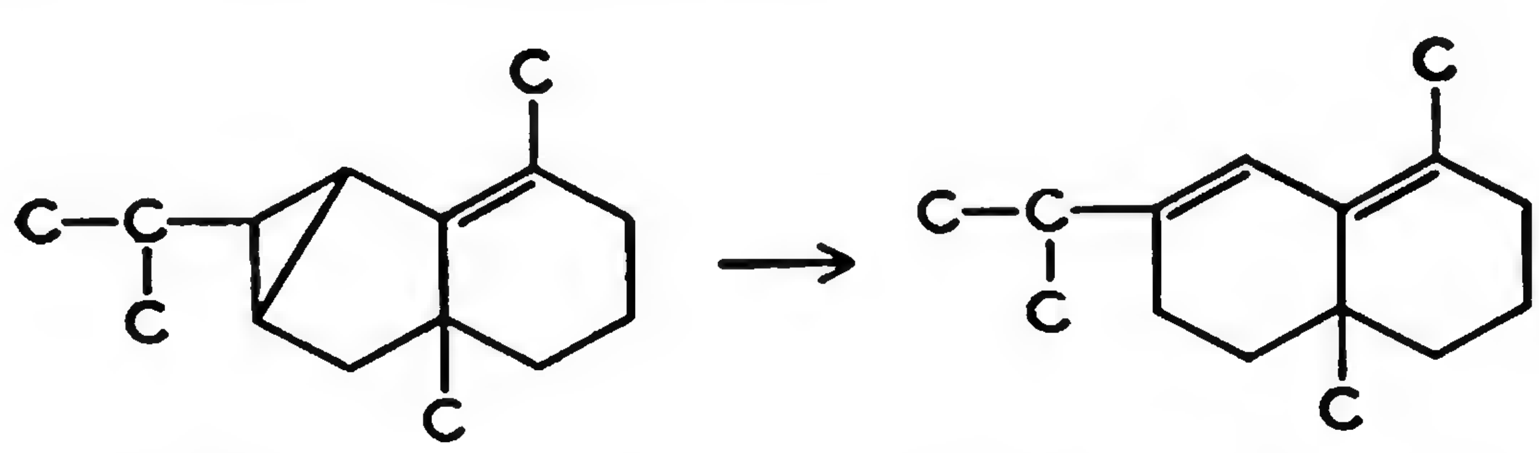
This reaction is accompanied by a slow dismutation into octahydro and tetradecahydro phenanthrenes.

Cedrene, heated under reflux with formic acid for several days, gave about 50 per cent of a lower-boiling tricyclic isomer.[469] Cedrene is definitely a tricyclene;[363] its structure is stated to be probably:



Cedrene [470]

l-α-Gurjunene (*i.e.*, *l*-tricyclene-gurjunene) when heated at 330° for 12 hours in a bomb tube formed *dl*-α-gurjunene and underwent a disproportionation into a monoterpene and diterpene.[536] *l*-α-Gurjunene, heated at 100° for 2 hours with acetic acid plus sulfuric acid, was decyclized to a bicyclic isomer, *l*-iso-α-gurjunene:[591]



l-α-Gurjunene *l*-Iso-α-gurjunene

d-β-Gurjunene (*i.e.*, *d*-tricyclo-gurjunene), treated with hydrogen chloride plus acetic acid, gave similarly the bicyclic, *l*-iso-β-gurjunene.[591] The structures of these two isomers are unknown.

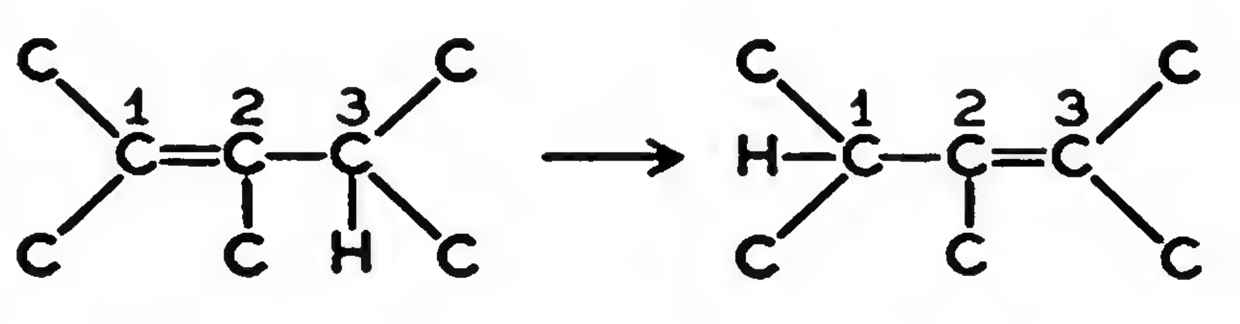
l-Sesquichamene is a tricyclic sesquiterpene of undetermined structure but known to be a tricyclene related to *d*-cedrene and *d*-β-gurjunene.[294, 363, 364] *l*-Sesquichamene, when treated for 1.5 hours with alcoholic sulfuric acid at 40-50°, gives *l*-isosesquichamene, which is a bicyclic isomer according to molecular-refraction measurement.[294]

Isomerizations of tricyclenes and tricyclenes with saturated side-chains are listed in Table 30, p. 352.

Conclusions

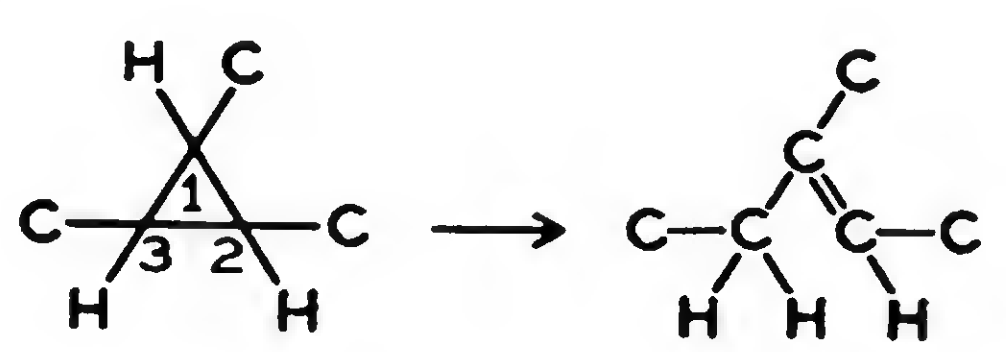
1. Isomerization of tricyclenes in two cases (with and without saturated side-chains) was accompanied by disproportionation, which is reflective of labile hydrogen behavior. Moreover, the isomerizations in these instances are also the result of hydrogen transfer.

2. $\Delta^{11,12}$-Dodecahydrophenanthrene exhibits isomerization by 1:3 hydrogen shift in the following manner:



(Skeleton structures)

3. Analysis of the isomerization of *l*-α-gurjunene indicates the same type of 1:3 hydrogen transfer in the decyclization of incorporated cyclopropane rings:

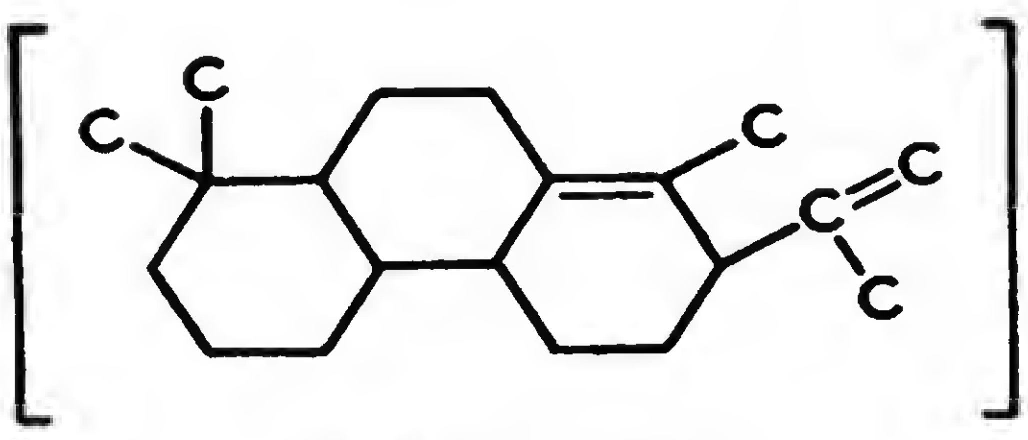


(Skeleton structures)

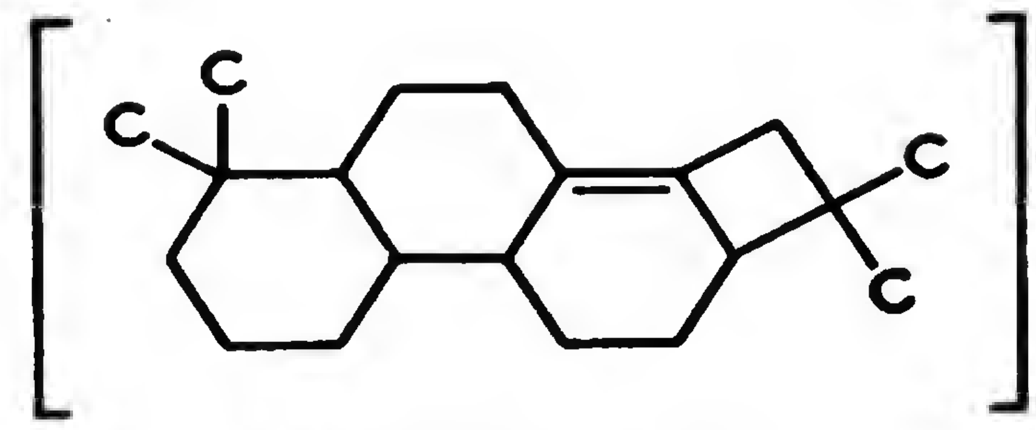
TRICYCLENES WITH UNSATURATED SIDE-CHAINS

Isomerizations

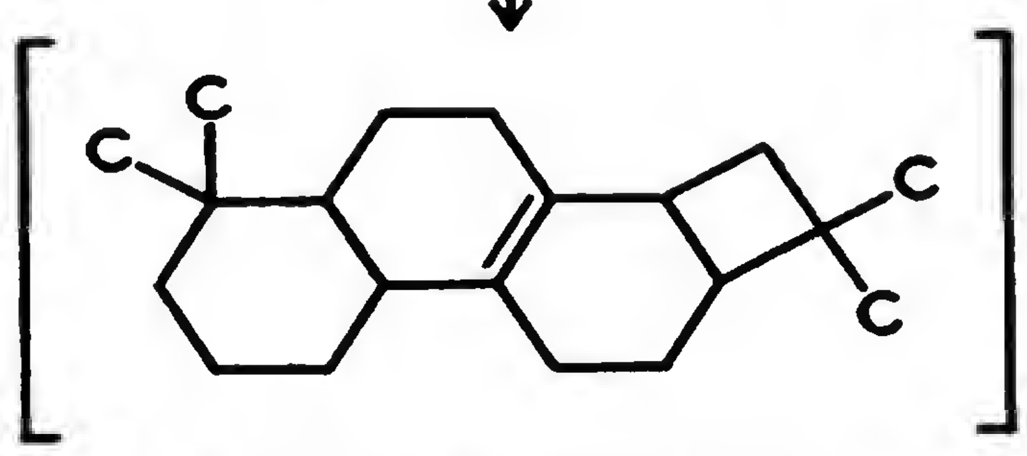
d-Rimuene, a diterpene or tricyclene with an unsaturated side-chain,[40, 87, 100] probably gives phyllocladene when heated alone to the boiling point,[367] and isophyllocladene when heated under reflux with formic acid for 48 hours.[40] The first step in the last isomerization is probably the formation of phyllocladene by cyclization.[87] It may be remarked that the formulas, proposed by various investigators, for rimuene,[40, 87] phyllocladene [90, 606] and isophyllocladene [606] are inconsistent, and introduce serious discrepancies in structures. The present authors suggest, for classification purposes, the following structures for rimuene, phyllocladene, and isophyllocladene, which are based upon related formulas for caryophyllene and clovene:



d-Rimuene



Phyllocladene



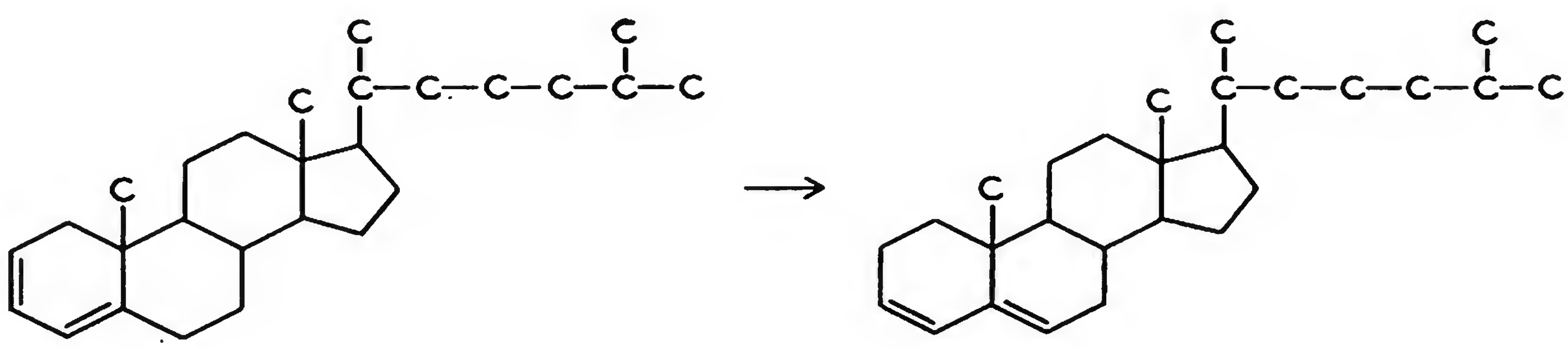
Isophyllocladene

These formulas, however, have the disadvantage of a deviation (isomerization) from the usual rule of 4 isoprene residues for diterpene structures. The experimental data are included as Table 31, p. 354.

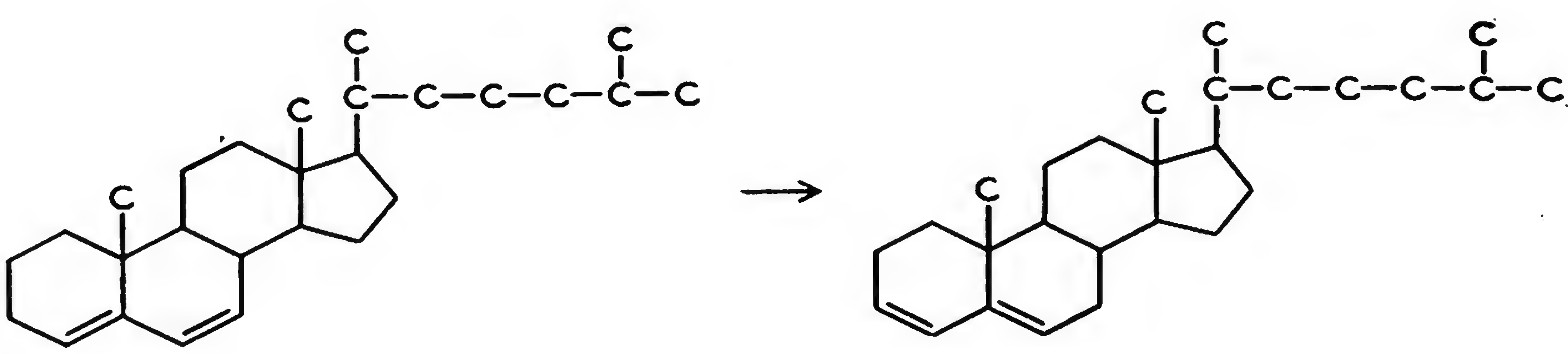
Tetracyclenes

Isomerizations

d-2,4-Cholestadiene is isomerized to *l*-3,5-cholestadiene (cholesterilene) by a treatment with alcoholic hydrochloric acid for 6-26 hours:[565]

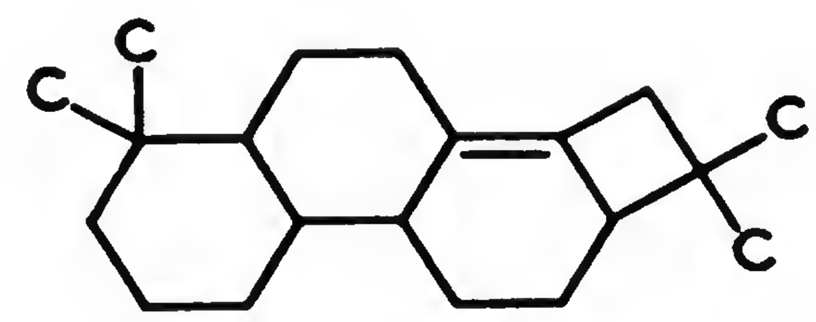


d-4,6-Cholestadiene gives *l*-3,5-cholestadiene when its solution in chloroform is subjected to hydrogen chloride gas for 3 hours:[150a]



The isomerization of *d*-phyllocladene (also known as dacrene or sciadopitene) into *d*-isophyllocladene (*i.e.*, isodacrene or isosciadopitene) takes place on heating at 100° with alcoholic sulfuric acid for a few minutes [90] or on boiling the mixture,[87, 90a, 409] Both isomers form the same hydrochloride, a fact that is indicative of the movement of a double bond during the isomerization.[87, 410] Phyllocladene is tetracyclic and probably contains the phenanthrene nucleus, an additional ring, and a double bond

(unlocated).[87, 90] The isomerization of phyllocladene (dacrene) occurred also at 800-900° under one mm. Hg absolute pressure, and as a result of treatments with formic, acetic, chromic, or nitric acids.[66]



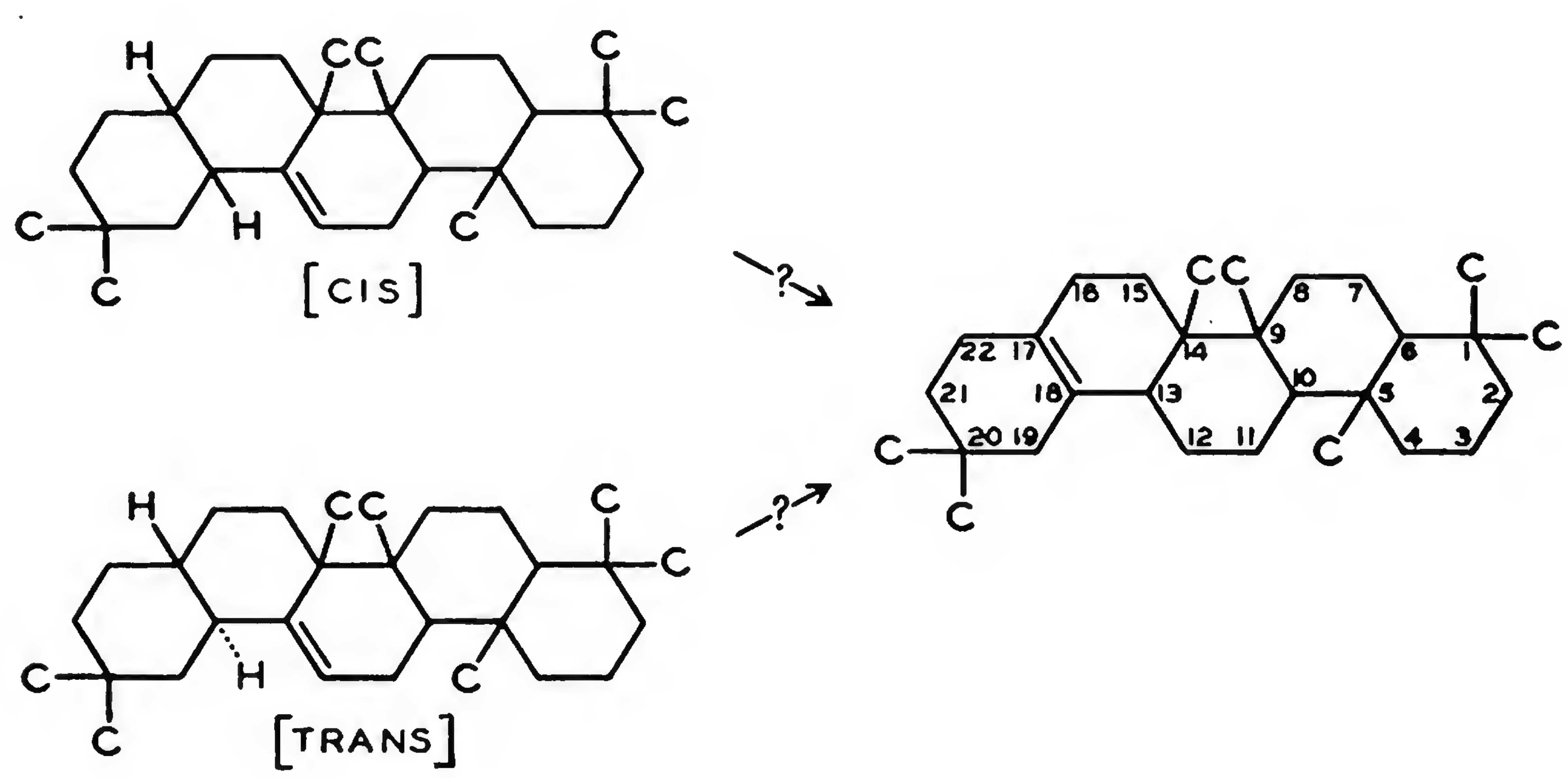
Phyllocladene
(Tentative structure based upon formulas for caryophyllene and clovene)

The isomerizations of the tetracyclenes are presented in Table 32, p. 354.

Pentacyclenes

Isomerizations

The isomerizations of two pentacyclenes, obtainable indirectly from oleanolic and quillaic acids, have been reported recently.[65a] *d*-17,18-cis-$\Delta^{12,13(?)}$-Oleanene and *d*-17,18-*trans*-$\Delta^{12,13(?)}$-oleanene were isomerized to $\Delta^{17,18(?)}$-oleanene when boiled with acetic acid containing hydrochloric acid and amalgamated zinc:



The number system of oleanenes and quillaic acid is retained by the present authors in order to avoid a possibly erroneous, though more systematic, eicosahydropicene classification. Table 33 (p. 354) gives further data on the foregoing isomerizations of pentacylenes.

Chapter VI

Aromatic Hydrocarbons

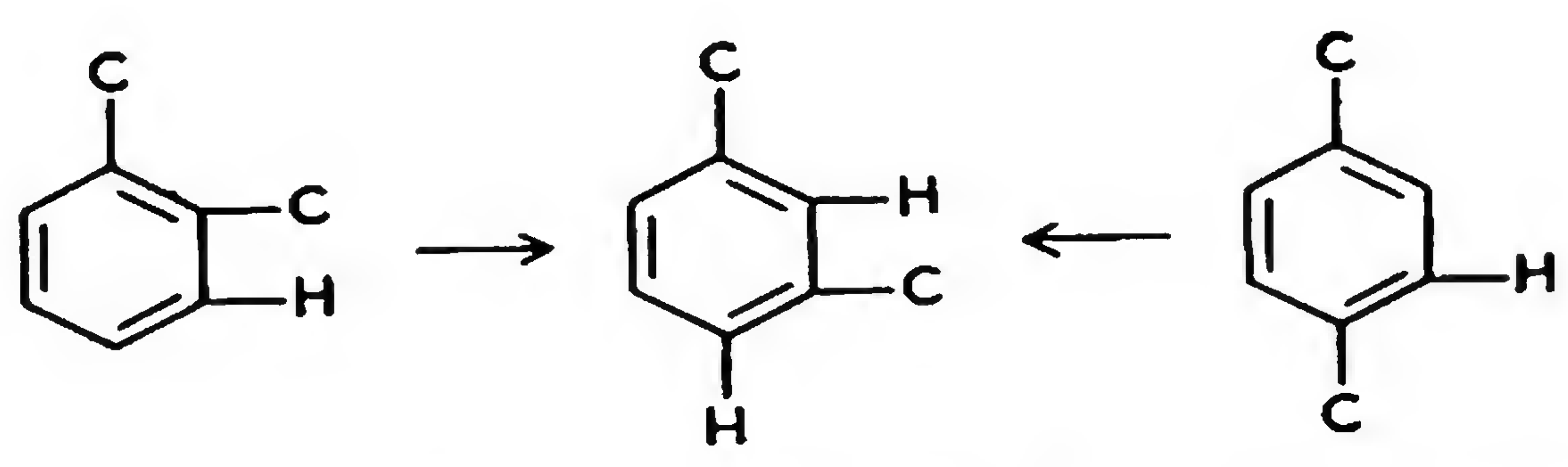
The number of observed isomerizations in the aromatics is large, though changes in the ring itself are seldom encountered. The isomerizations of aromatics observed to date can be explained generally by certain non-aromatic hydrocarbon reactions, such as hydrogen migration, formation of alkyl, alkenyl, and alkylidene radicals; intermediate-product formation; and cyclization plus decyclization. The aromatic hydrocarbons will be considered in the structural order: alkyl benzenes, alkenyl benzenes, alkadienyl benzenes, alkapolyenyl benzenes, alkynyl benzenes, indenes, naphthalenes, anthracenes, phenanthrenes, highly-condensed aromatics, aromatic-cyclane hydrocarbons, and aromatic-cyclene hydrocarbons.

Alkyl Benzenes

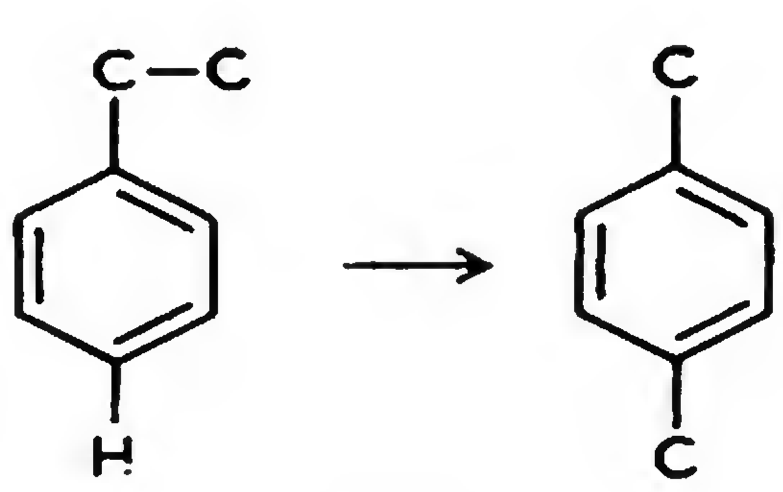
Mechanism

The alkyl benzenes, or monocyclic aromatic hydrocarbons with saturated side-chains, can be expected to undergo several types of isomerization. Four of these types are well-known or expected instances occurring by *changes outside of the ring:*

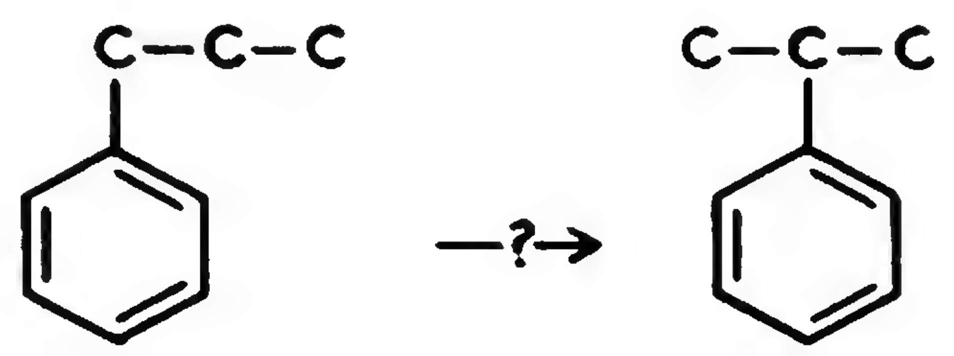
1. Isomerization by shifting of intact alkyl groups along the ring. This requires the following over-all changes: dehydrogenation (one hydrogen only) plus dealkylation, and a subsequent alkylation plus hydrogenation. An exchange in the position of alkyl and hydrogen takes place:

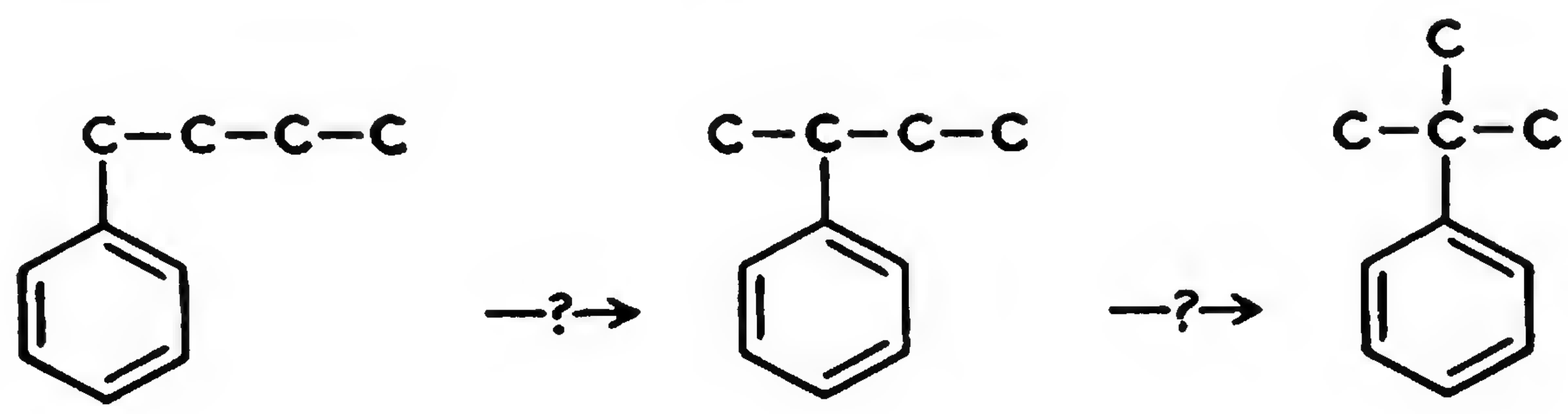


2. Isomerization by rupture within the side-chain, followed by a distribution of the new radical, or new radicals, along the ring. The over-all changes are dehydrogenation (one hydrogen only) at the ring plus scission within side-chain, followed by alkylation plus hydrogenation, *e.g.*:



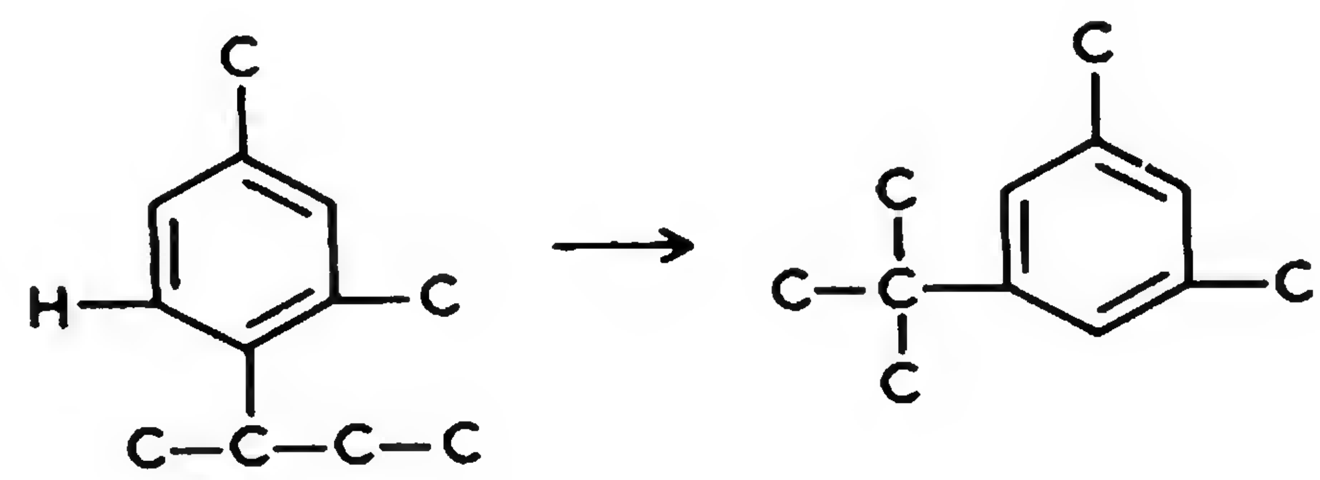
3. Isomerization within the side-chain itself, consisting of ruptures therein and the formation of a more symmetrical side-chain:





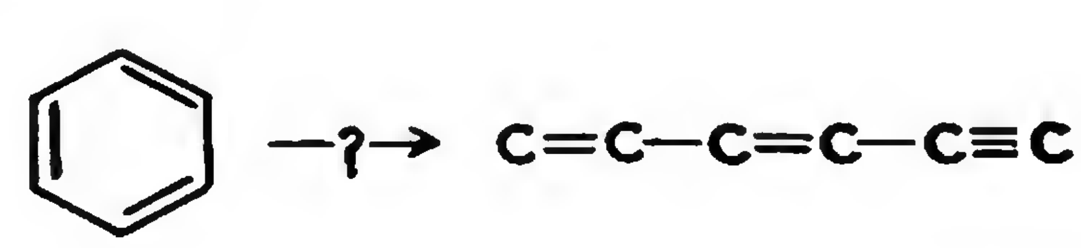
This isomerization has not been observed to date.

4. Isomerization by shifting of rearranged alkyl groups along the ring. The over-all changes required are: dehydrogenation plus dealkylation plus rearrangement of alkyl, and a subsequent alkylation plus hydrogenation. An exchange in position of the single hydrogen and new alkyl occurs. This shift can be considered a combination of types 1 and 3:

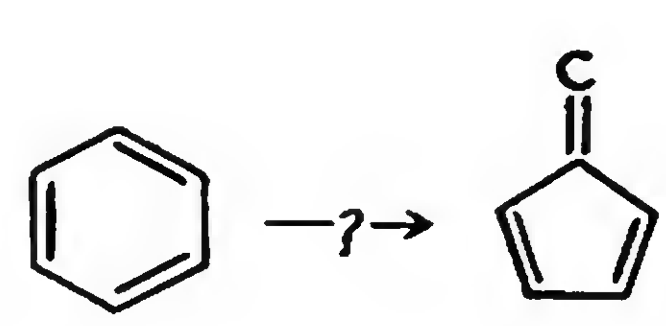


Besides these 4 types, there are 4 kinds of isomerization involving ring changes that can be expected under unusual reaction conditions. In the following types, the postulated products are still to be isolated via isomerization, although hexadien-1,3-yne-5, substituted fulvenes, and "semi-benzenes" are known.

5. Opening of the ring with the formation of extremely reactive straight-chain unsaturated hydrocarbons, for example:

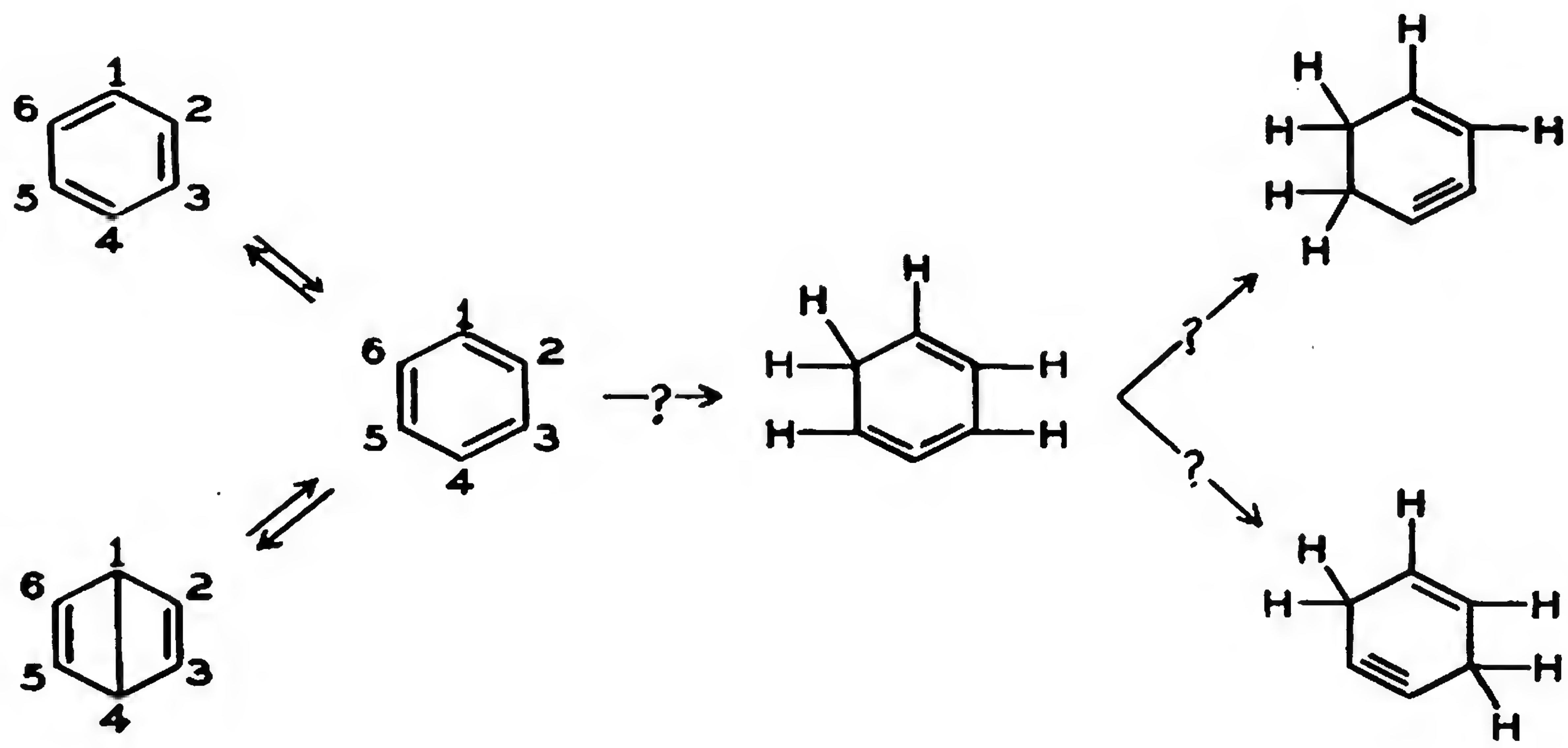


6. Opening of the ring with subsequent closure to form a reactive fulvene:

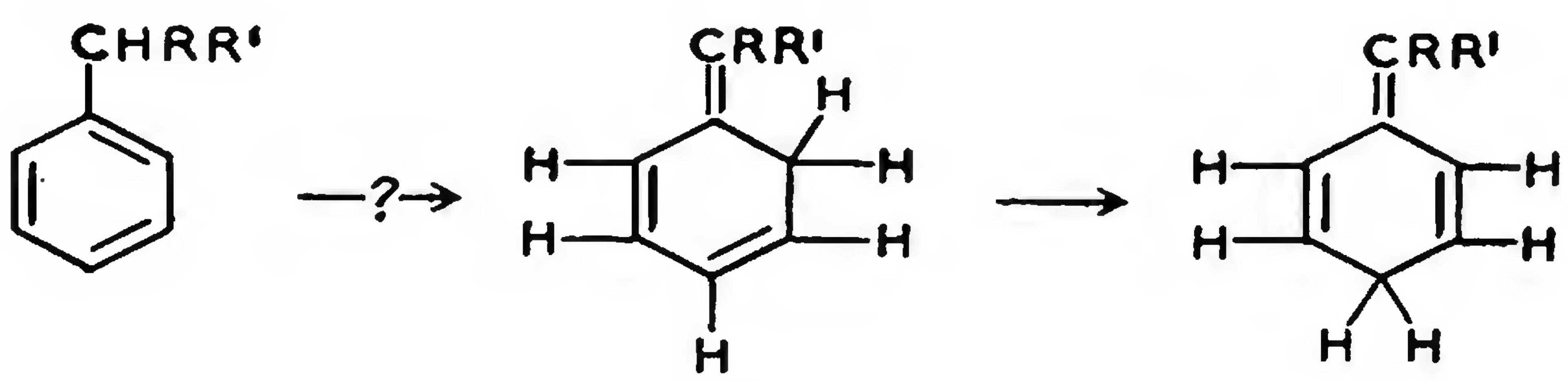


7. Changes of the type of bonds present *within the ring, i.e.*, converting aromatic bonds into allenic, triple bond, and para-bond types. The

cyclic alkene-allene and cyclic alkene-alkynes seem to be ruled out for stereochemical reasons:



8. Shift of a double bond into the side-chain:



Many more hypothetical isomerizations could have been included. Only those encountered at times in the literature have been given as illustrations.

Isomerizations

There is no direct experimental evidence of isomerization according to types 5, 6, and 7. This may be due to extreme reactivity of the unsaturated products, to unfavorable states of equilibrium, or to stereochemical barriers preventing their formation. However, benzene reacting with aluminum chloride gives alkyl benzenes, showing that the ring does break up; benzene when heated at 180-200° for 48 hours with 20 per cent of aluminum chloride gave toluene and ethylbenzene.[196] The action of aluminum chloride (10 per cent) plus dry hydrogen chloride on benzene, at 125° for 24 hours in a closed autoclave, gave 1.7 per cent of ethylbenzene.[280]

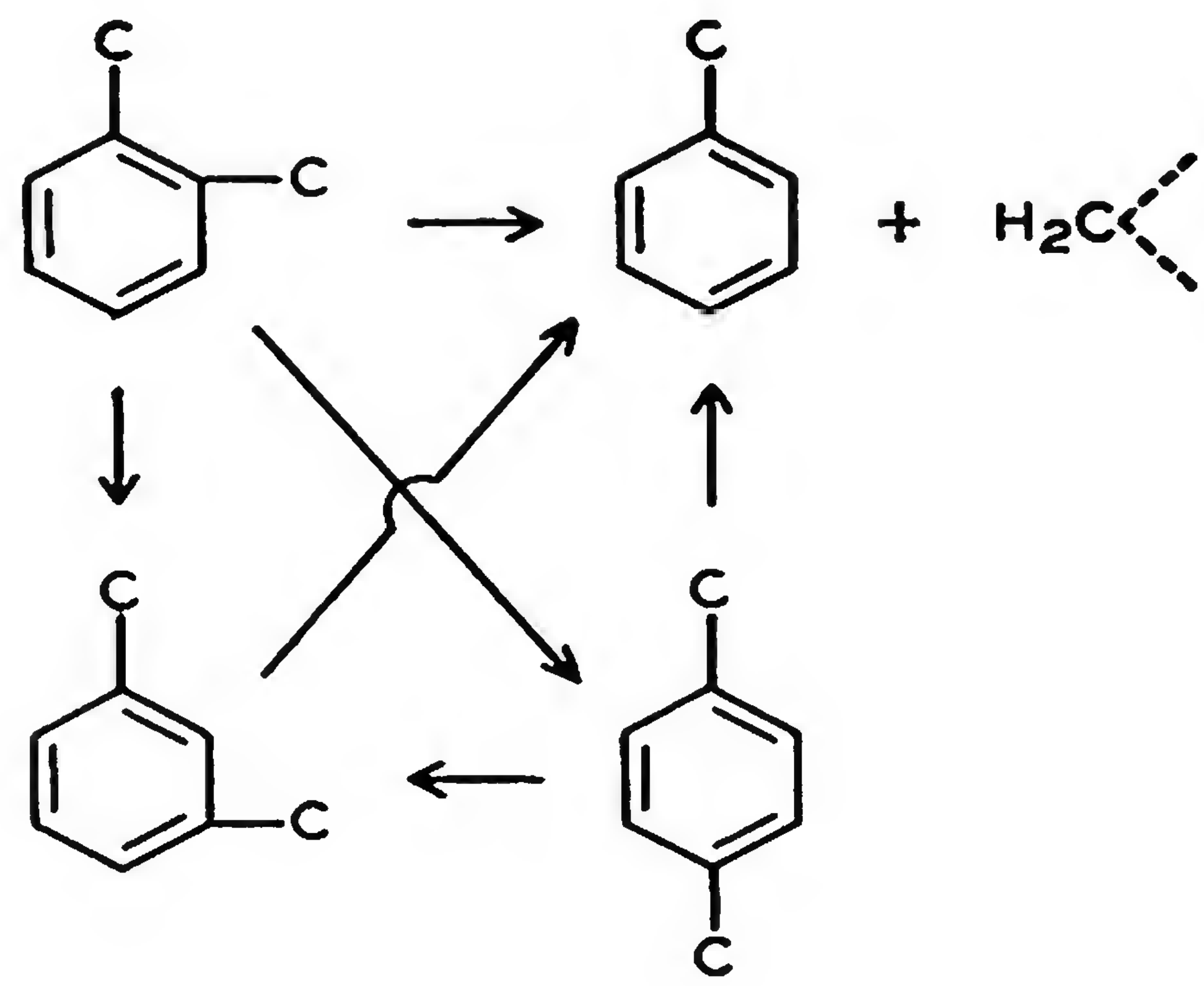
A study of the ultraviolet absorption spectrum of toluene (the simplest member of a group of toluenes corresponding to the last postulated type of isomerization) at 67° revealed the appearance of new (methylene) lines. This can be explained by the tautomerization of toluene into a form containing a double bond outside of the ring.[376] The corresponding change of 1-methylcyclohexene-1 into methylenecyclohexane has been considered already under the Cyclenes.

The dimethylbenzenes (xylenes) undergo isomerization by a shift of methyl groups along the ring.[6, 7, 245, 392, 414, 415] This reaction occurred under the catalytic action of aluminum chloride plus hydrogen chloride for 10 minutes at 55° [414] or for 5 hours at 50°,[415] also for 15 minutes at 94° [415] or for 6 hours at 100°,[245] producing much *m*-xylene. It has been pointed out (a) that changes in temperature affect the relative proportions in which isomers are formed from the xylenes; (b) that a decrease in the molecular ratio of aluminum chloride to xylene decreases the isomerization rate and the percentage of decomposition; and (c) that hydrogen chloride increases the decomposition without changing the relative proportions of isomers.[415] The effects of structure of the initial xylenes, contact time, and temperature upon the composition of the entire final product are brought out in Table 34.

Table 34. Isomerization of Xylenes by Aluminum Chloride (55.7%) in the presence of Hydrogen Chloride.[415]

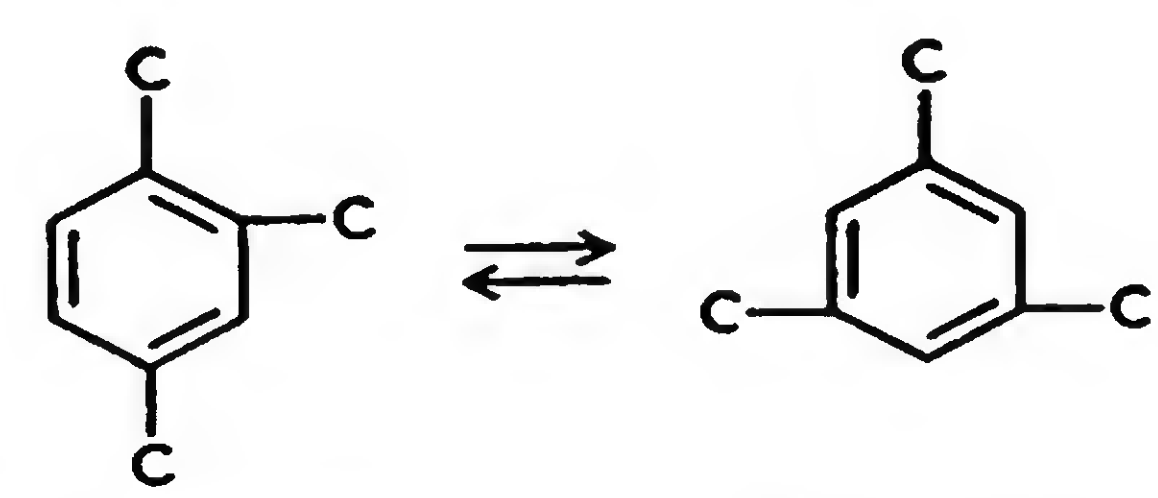
Starting Material (Reacting Xylene)	Reaction Conditions		Percentage of Products		
	Contact Time (hours)	Temp. (°C.)	*o*-Xylene	*m*-Xylene	*p*-Xylene
ortho	5	50	<37.6	<51.7	<4.7
ortho	0.25	94	<31.9	<38.6	<13.4
meta	0.5	50	0(?)	89.2(?)	2.8
meta	1.5	50	15	72.4	6.6
meta	5	50	11.7	61.9	10
meta	18	50	12.9	55.7	12.1
meta	20	50	<16	<69	<15
meta	30	50	12.5	53.9	12.1
meta	48	50	11.1	46.6	11.8
meta	50	50	<12.8	<53.6	<14.4
meta	75	50	10.2	41.7	12.2
meta	0.25	94	<18	<72	<10
para	5	50	<11.6	<63.1	<8.3
para	0.25	94	<14.4	<27.9	<47.7

In Table 34, the percentage of isomer products is given for 1:1 molar initial concentrations of xylene and aluminum chloride (in the presence of hydrogen chloride).[415] Complexes of aromatics with aluminum chloride (a large number of which have been described) probably play an important role in such isomerizations.[160, 412, 414, 416] The thermal isomerization of *o*- and *p*-xylenes in a porcelain tube at 700-770° gave respectively 76.3-22.5 and 0.0 per cent of *o*-xylene, 4.0-16.8 and 1.2-4.1-3.8 (4.1 = maximum) per cent of *m*-xylene, trace-4.6 and 88.2-45.4 per cent of *p*-xylene, along with 4.6-12.8 and 2.1-13.3 per cent of toluene, 12.1-25.4 and 6.9-19.3 per cent of "condensed products," and 2.1-14.8 and 0.9-14.8 per cent of gas.[139] *m*-Xylene gave 1.7-15.4 per cent of toluene under the same conditions, but was not isomerized. *p*-Xylene gave 3.3 per cent of crude *m*-xylene when passed through a quartz tube at 800°.[28] It is possible that "demethylation" to toluene proceeds concurrently with, and more or less independently of, these isomerizations:



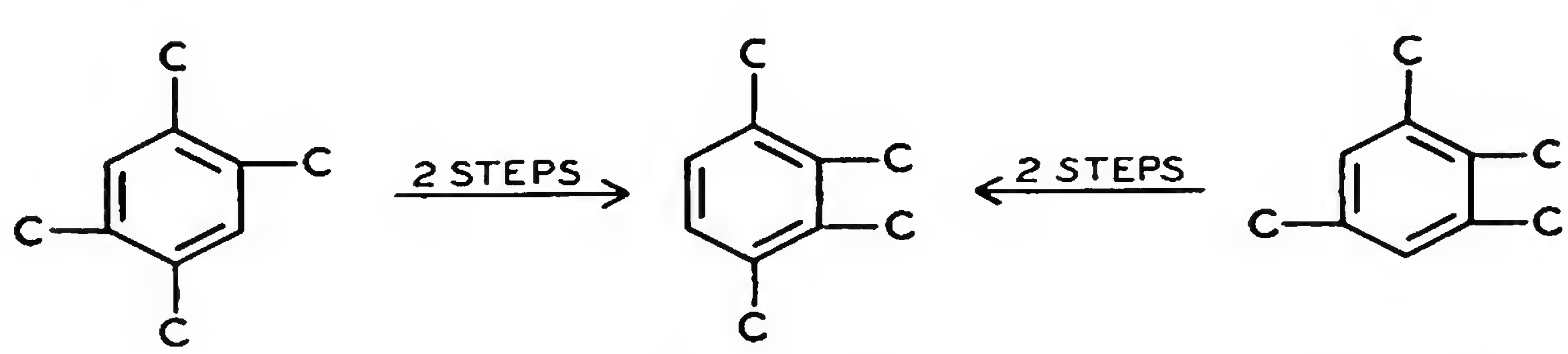
It is interesting to note the following facts concerning the stability of C_8H_{10} aromatics. *o*- and *p*-Xylenes isomerized mainly to the meta derivative, just as did the corresponding cyclohexanes. Ethylbenzene did not isomerize to xylenes in the presence of aluminum chloride at 100° or 136°.[245] However, ethylbenzene when passed slowly through a "moderately red"-hot porcelain tube formed styrene and smaller amounts of benzene, toluene, *p*-xylene, and naphthalene.[61, 63] The observed small amount of *p*-xylene may be due to secondary reactions, but when considered together with other findings, it warrants an investigation of the stability of the ethyl group at the center of the chain.

The polyalkyl aromatics also show the first type of isomerization. 1,2,4-Trimethylbenzene (pseudocumene), in the presence of aluminum chloride at 150-160°, gave 1,3,5-trimethylbenzene (mesitylene), and vice versa:[290]



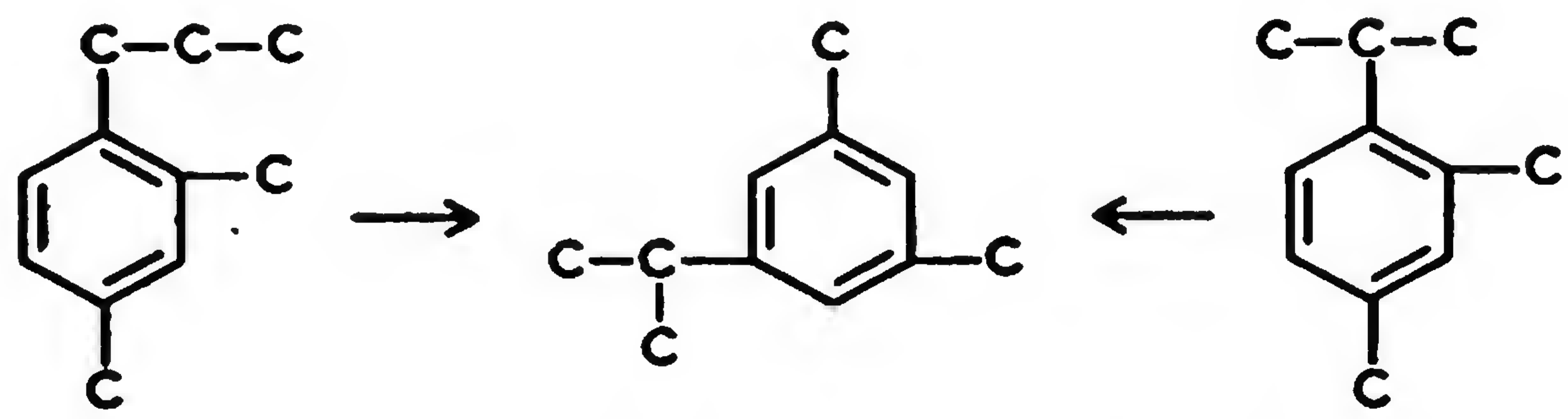
Pseudocumene Mesitylene

1,2,4,5-Tetramethylbenzene (durene) and 1,2,3,5-tetramethylbenzene (isodurene) formed 1,2,3,4-tetramethylbenzene (prehnitene) when sulfonated in the presence of sulfuric acid and subsequently hydrolyzed.[558] A flash system of hydrolysis (at 140-150°) by dilute sulfuric acid and superheated steam was utilized:[560]

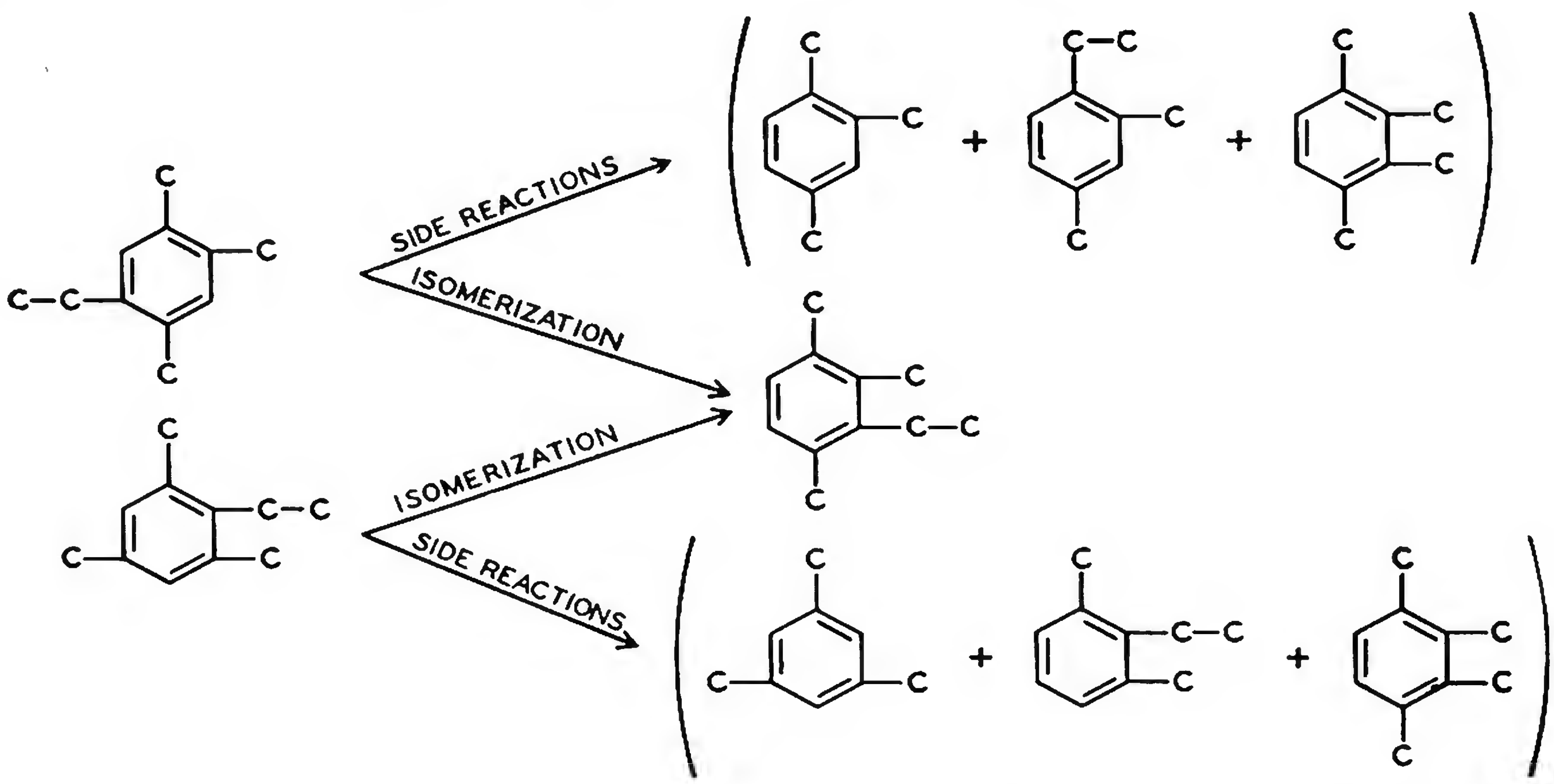


Durene Prehnitene Isodurene

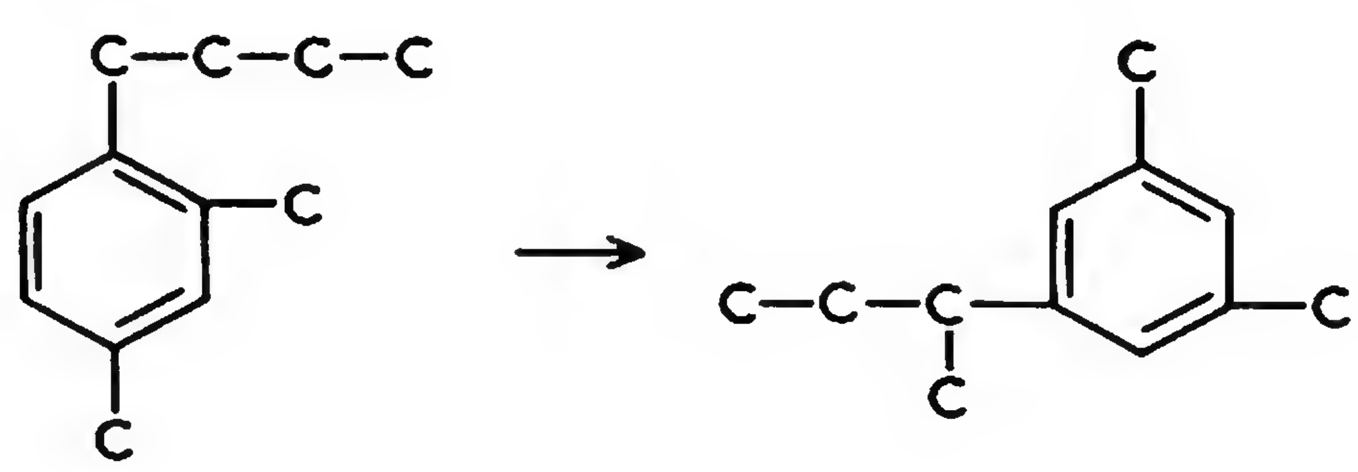
The treatment of 1-*n*-propyl-2,4-dimethylbenzene (*i.e.*, "1,3-dimethyl-4-*n*-propylbenzene") and of "1,3-dimethyl-4-isopropylbenzene" with aluminum chloride at 100° and 55-60°, respectively, yielded 1,3-dimethyl-5-isopropylbenzene:[404]

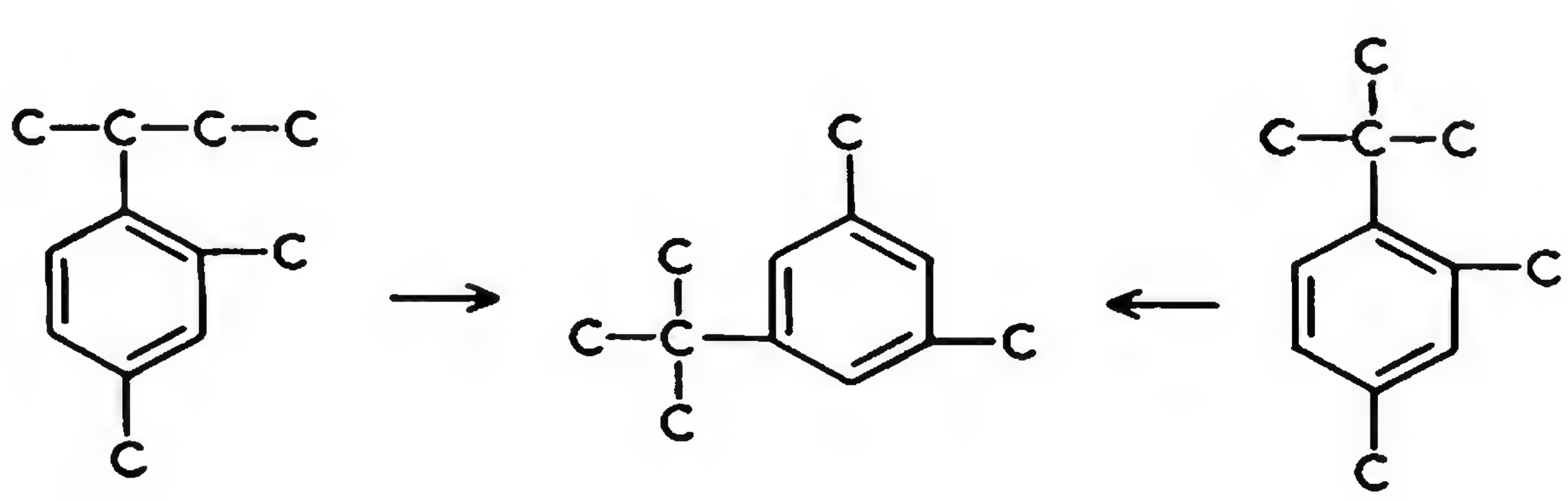


1,2,4-Trimethyl-5-ethylbenzene and 1,3,5-trimethyl-2-ethylbenzene isomerized respectively to 27.0 and 34.5 per cent of 1,2,4-trimethyl-3-ethylbenzene when subjected to sulfonation at 60-70° and desulfonation at 140-150°.[559] The isomerizations are accompanied by side reactions:

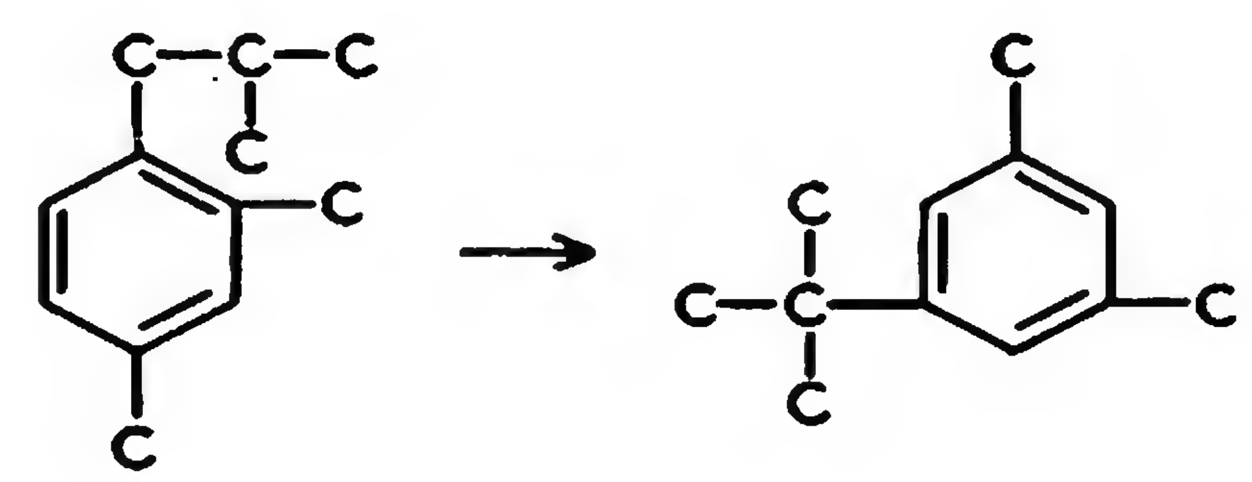


1-*n*-Butyl-2,4-dimethylbenzene (*i.e.*, "1,3-dimethyl-4-*n*-butylbenzene") gave 1,3-dimethyl-5-*sec*-butylbenzene when warmed with aluminum chloride, whereas the heating of either "1,3-dimethyl-4-*sec*-butylbenzene" or "1,3-dimethyl-4-*tert*-butylbenzene" with aluminum chloride resulted in the formation of 1,3-dimethyl-5-*tert*-butylbenzene:[405]

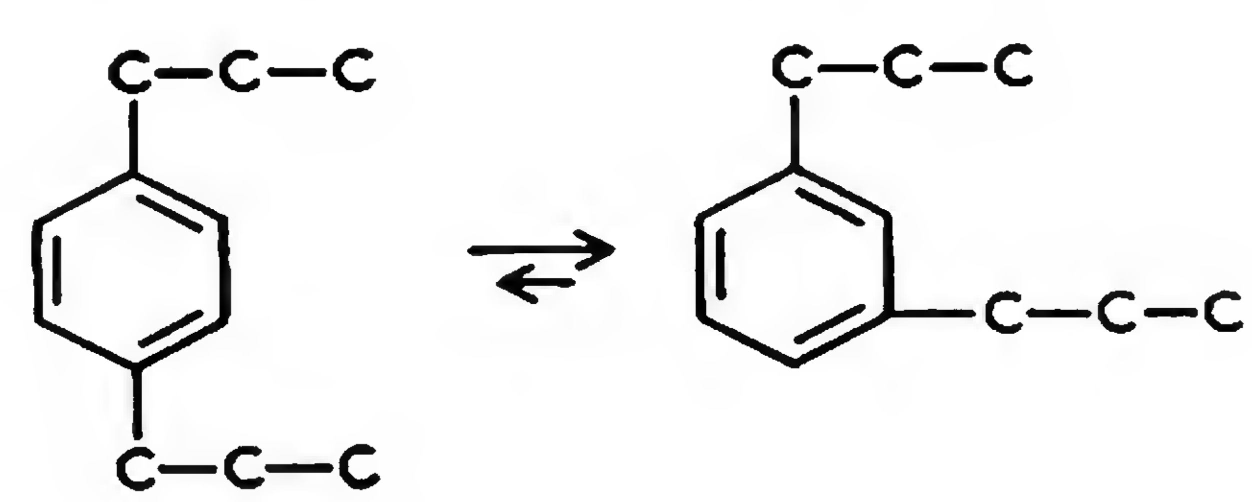




About 10 per cent of *m*-xylene was formed also, along with high-boiling (higher-alkylated?) hydrocarbons. A 45 per cent yield of 1,3,5-isomer from "1,3-dimethyl-4-*tert*-butylbenzene" has been reported;[561] whereas the yields of 1,3,5 isomers from the "1,3-dimethyl-4-butylated benzenes" varied from 20-60 per cent.[405] "1,3-Dimethyl-4-isobutyl benzene," treated similarly with aluminum chloride, gave a "mixture" of hydrocarbons.[405] Ferric chloride is a better catalyst than aluminum chloride for isomerizations of the "1,3-dimethyl-4-butylated benzenes." [405a] The treatment of "1,3-dimethyl-4-isobutylbenzene" with anhydrous ferric chloride for 2.25 hours at 80-110° gave about 52 per cent of 1,3-dimethyl-5-*tert*-butylbenzene:

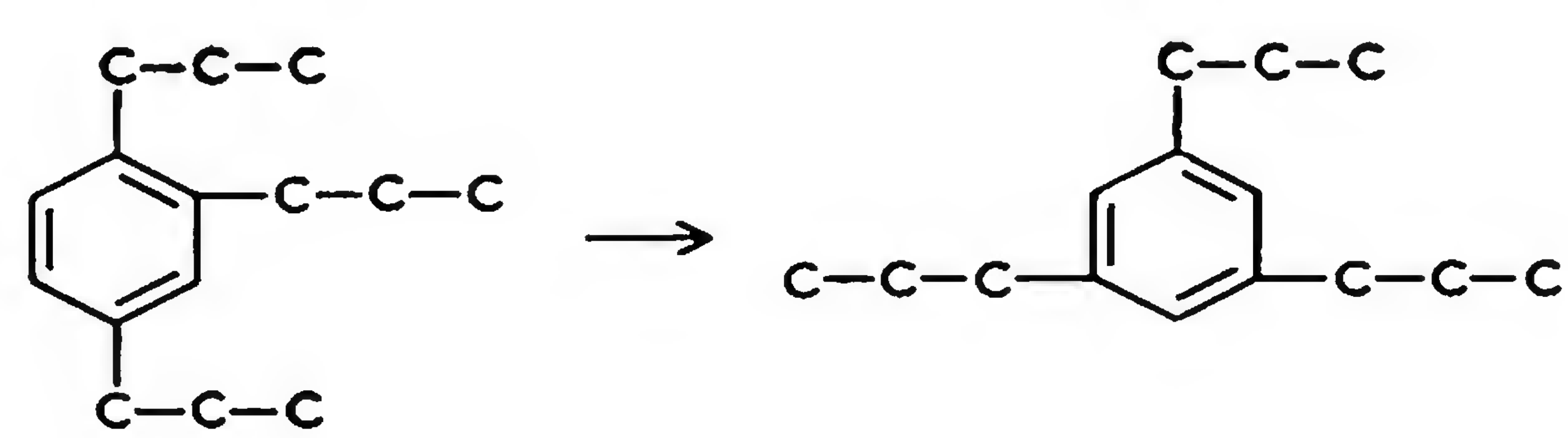


In isomerizations with aluminum chloride at 100°, *p*-dipropylbenzene yielded 66.7 per cent of *m*-dipropylbenzene in 2 hours (dropping to 15.7 per cent in 22 hours), whereas *m*-dipropylbenzene formed only a small amount of the para compound when similarly treated for 22 hours:[27]



1,2,3,5-Tetraethylbenzene and 1,2,4,5-tetraethylbenzene were converted into 1,2,3,4-tetraethylbenzene by sulfonation with sulfuric acid at 100°, followed by hydrolysis at 130-150° in the presence of "50 per cent sulfuric acid" and steam.[558a] These indirect isomerizations are analogous to those of isodurene and durene, which form prehnitene, but the present yields are considerably higher (over 85 per cent).

1,2,4-Tripropylbenzene formed 28 per cent of 1,3,5-tripropylbenzene when treated with aluminum chloride for 4 hours at 100°: [27]

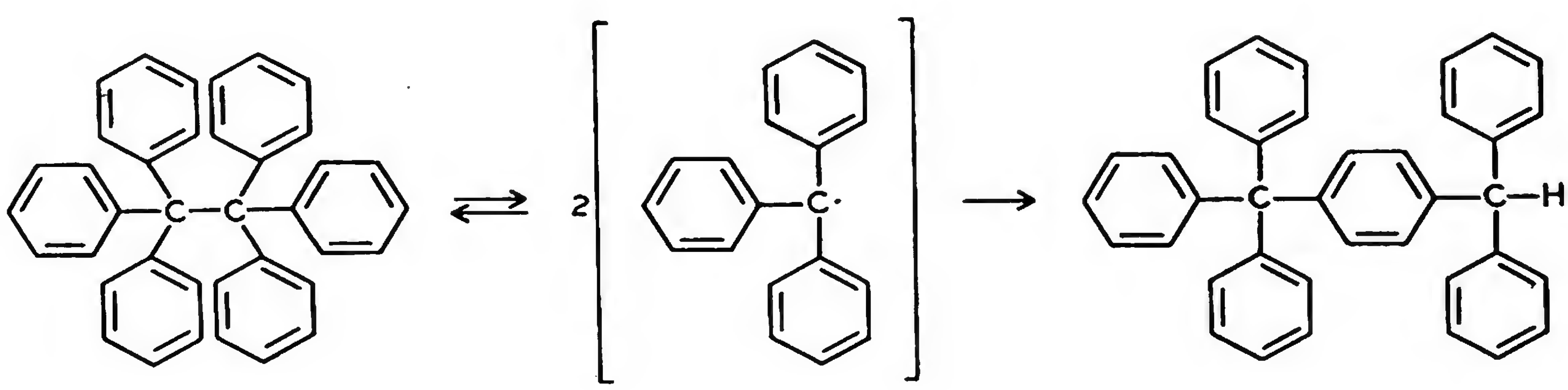


Some doubt [405] has been expressed about the "normal character" of the migrating propyl group, since isopropyl groups would be formed by a

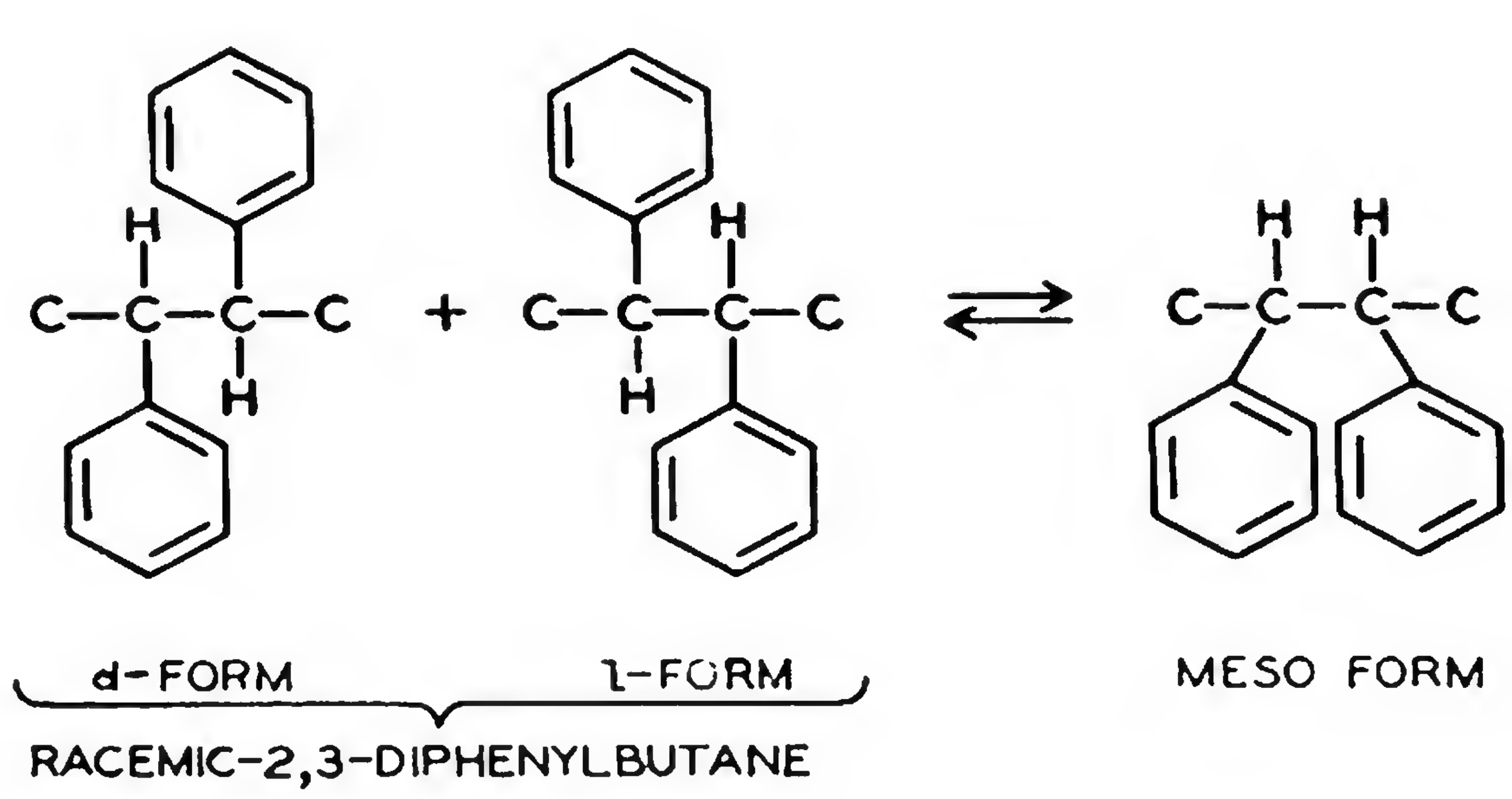
side-chain isomerization. The foregoing isomerizations [27] were accompanied by the formation of lower- and higher-propylated products, which represents drastic reaction conditions for an intact migration of *n*-propyl groups.

Triphenylmethane has been described as occurring in stable (m.p. 92°) and unstable (m.p. 81°) forms,[207] as well as in a labile form (m.p. 92.5°, uncorrected).[233] The labile form, when heated at 75-80°, gives the stable form (m.p. 92.5°, uncorrected), but it is very uncertain whether an isomerization of triphenylmethane takes place.

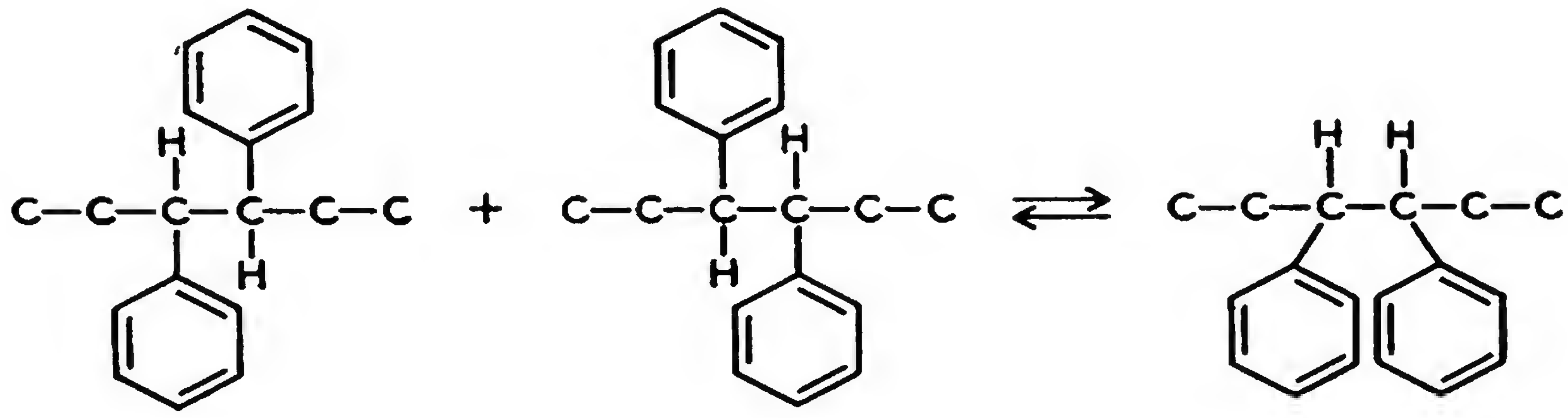
Hexaphenylethane [223, 593] is another example of an aromatic containing several phenyl groups. It has been isomerized into *p*-benzohydryl-tetraphenylmethane by (a) treatment (in benzene solution) with small amounts of hydrogen chloride gas [222] or hydrochloric acid,[222] by (b) heating with *m*-xylene,[646] and by (c) treating the ether solution of "triphenylmethyl" with sodium.[519] The formation of *p*-benzohydryl-tetraphenylmethane involves the formation, isomerization, and recombination of intermediary free radicals:



2,3-Diphenylbutane is known in a liquid (*dl*) and in a solid (meso) form; the liquid form is converted into the latter when heated at 235-250° for 8 hours:[334]



3,-4-Diphenylhexane exists in a liquid (*dl*) and in a solid (meso) form, partly convertible into each other by heating with iodine at 250-265° in a sealed tube: [335]



d-FORM l-FORM MESO FORM

RACEMIC-3,4-DIPHENYLHEXANE

Isomerizations of alkyl benzenes are listed in Table 35, p. 356.

Conclusions

1. Reactions of types 1 (shift of intact alkyl groups), 2 (new alkyls via rupture within side-chains), and 4 (shift of rearranged alkyl groups) are accompanied by the formation of lower- and higher-alkylated aromatics, which indicates a complete rupture of some side-chains from the initial hydrocarbons. This favors also a complete rupture in the "event" of isomerization. The detached groups may react with the ring as free radicals, or as alkenes causing alkylation (especially where the side-chains undergo an isomerization).

2. The conversion of racemic diphenyl alkanes into meso forms is an isomerization that should find numerous analogies. In fact, all monophenyl alkanes, in which a suitable alkyl replaces one of the phenyl groups of such diphenyl alkanes, may undergo this isomerization.

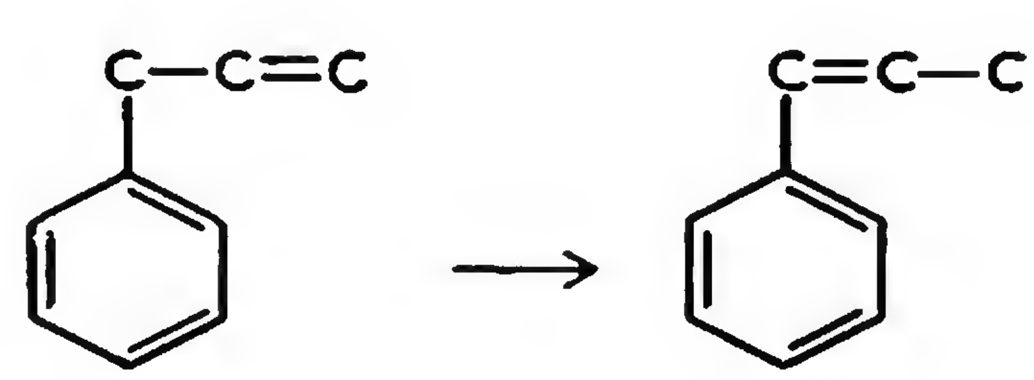
3. Recombination, rather than isomerization, of aromatic free radicals has been studied; formation of free radicals from the highly arylated ethanes is a very general reaction.

Alkenyl Benzenes

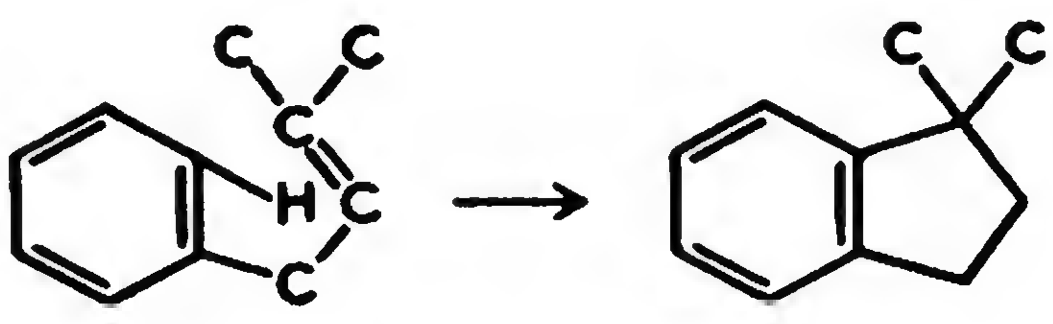
Mechanism

The alkenyl benzenes, or monocyclic aromatic hydrocarbons with alkenyl side-chains, can be expected to undergo more complex isomerizations than those observed in the case of alkyl benzenes. The following types of changes are often encountered:

1. Shifting of double bonds within the side-chain:



2. Cyclization, or "internal alkylation," by closure upon an unsaturated side-chain:



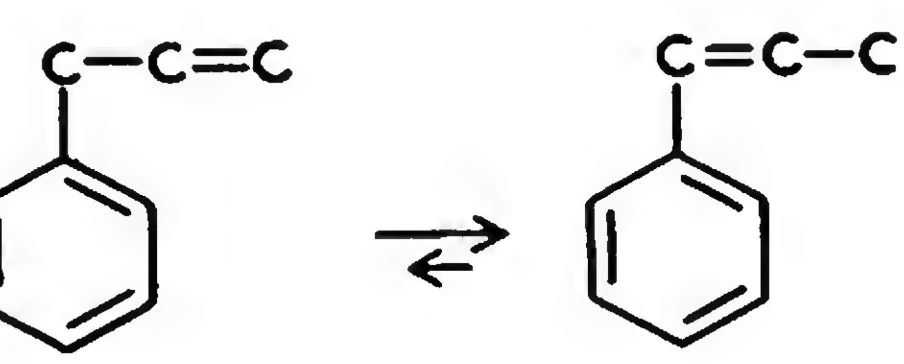
3. *Cis-trans* isomerization in unsaturated side-chains.

The isomerizations effected by changes within unsaturated side-chains attached to benzene are reactions that are characteristic of the alkenes. These isomerizations take place on heating, or by the use of various catalysts.

Isomerizations

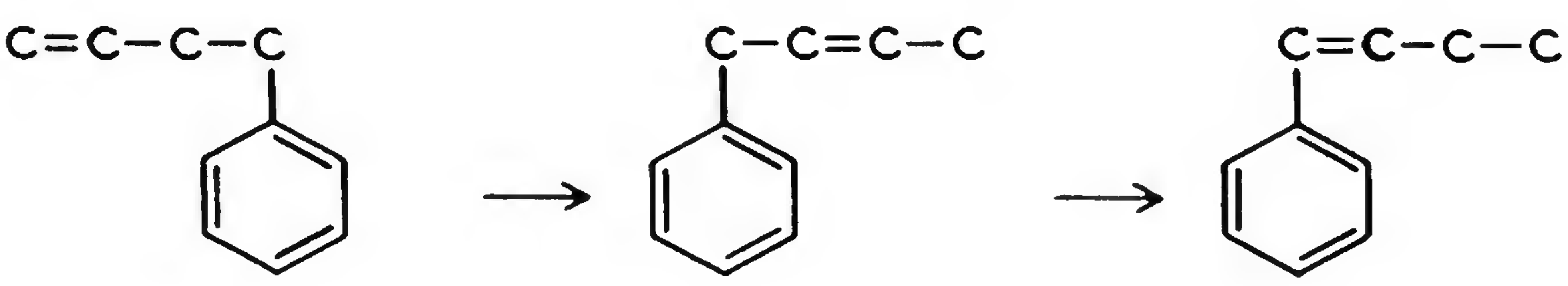
The alkenyl benzenes discussed in this section are arranged in order of increasing size of side-chain. Phenylated alkenyl benzenes are also considered at this point, because their isomerizations are related to those of the alkenyl benzenes.

Allylbenzene gave propenylbenzene when heated in the presence of dry caustic alkalies,[2] alcoholic potash,[309, 584] chromia or ferric oxide at 220°,[339] alumina at 220-225°,[338] palladium at 300°,[348] charcoal, silica gel, or clay at 300°,[339] nickel on asbestos at 360°,[338] or infusorial earth at 500°.[456, 457] The reaction with dry caustic alkali is reversible:[2]

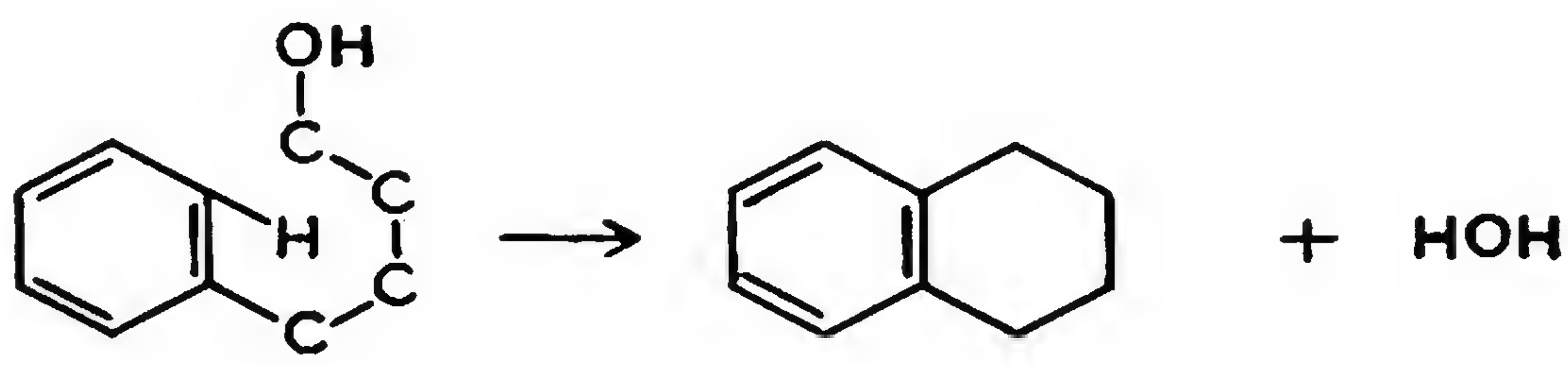


Obviously, no single mechanism can explain the formation of propenylbenzene under the various reaction conditions. The isomerization bears a similarity to that of the thermal conversion of allylcyclohexane into propenylcyclohexane.

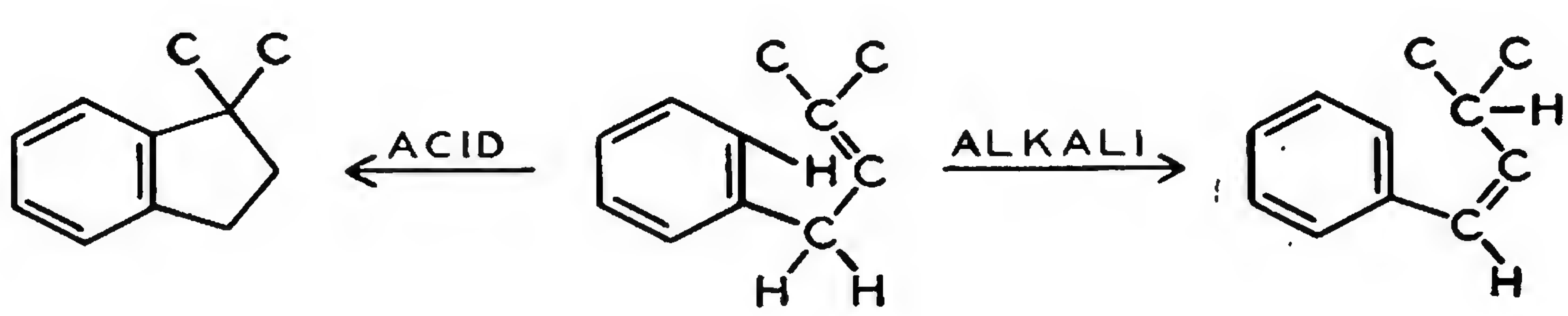
4-Phenylbutene-1 probably isomerized into a small amount of 1-phenylbutene-1 and 1-phenylbutene-2, when passed with carbon dioxide through a "Pyrex" tube at 550°.[261, 262] Passage of 4-phenylbutene-1 (with carbon dioxide) over platinum at 300° yielded these products.[345] 4-Phenylbutene-1 formed a catalyzate with 80-93 per cent of 1-phenylbutene-1 when conducted over alumina at 225-300° in a stream of carbon dioxide.[346a] The last workers found chromia to be a suitable catalyst at 225-250° for the same reaction and pointed out the conjugation of the product's side-chain and ring double bonds. The side-chain double bond probably migrates stepwise toward the ring:



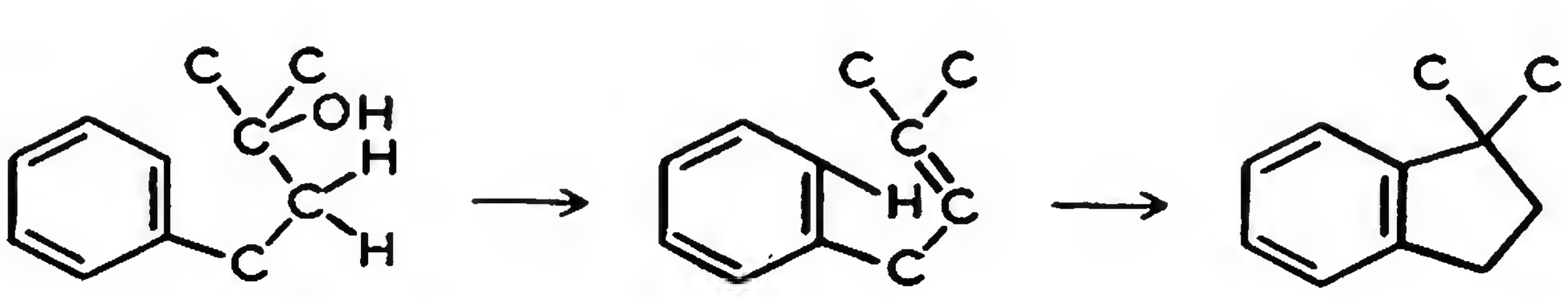
This interpretation of the reaction is substantiated by the formation of 1-phenylbutene-1 when 1-phenylbutene-2 is either boiled with alcoholic potash,[183] or heated at 160-180° with it in a bomb for a long time.[308] Attempts [72] to cyclize 4-phenylbutene-1 with the aid of acidic catalysts were unsuccessful, owing to the development of polymerization or other side reactions. Moreover, the cyclodehydration of 4-phenylbutanol using 85-per cent phosphoric acid, which gives the desired tetrahydronaphthalene, appears to be only a simple dehydration:[72]



1-Phenyl-3-methylbutene-2 underwent cyclization to 1,1-dimethylindane when treated with strong sulfuric acid or 85-per cent phosphoric acid.[72] This is an isomerization of an alkene-aromatic by an intramolecular alkylation. It proceeds mainly on account of the alkene-like properties of the initial hydrocarbon. 1-Phenyl-3-methylbutene-2, when heated at 180° with alcoholic potash, gave 1-phenyl-3-methylbutene-1.[308] Under the opposing conditions caused by the presence of acid or alkali, the transfer of the labile hydrogen atoms of 1-phenyl-3-methylbutene-2 is highly selective:

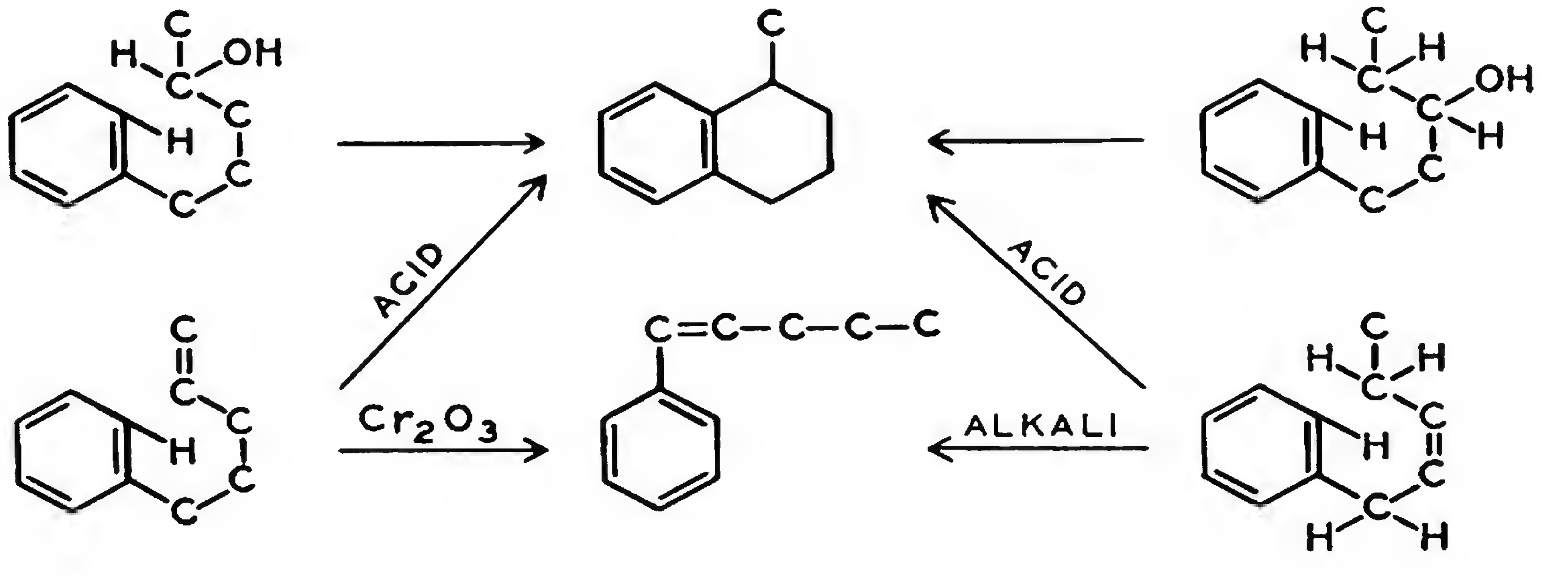


The cyclodehydration of aromatic alcohols in some cases appears to involve the intermediary formation of alkenes. The latter subsequently undergo a cyclization of the type exhibited by 1-phenyl-3-methylbutene-2, but probably polymerize also.[72] Dimethylphenethylcarbinol, upon treatment with hot 85-per cent phosphoric acid, definitely undergoes a cyclodehydration via isomerization as follows:

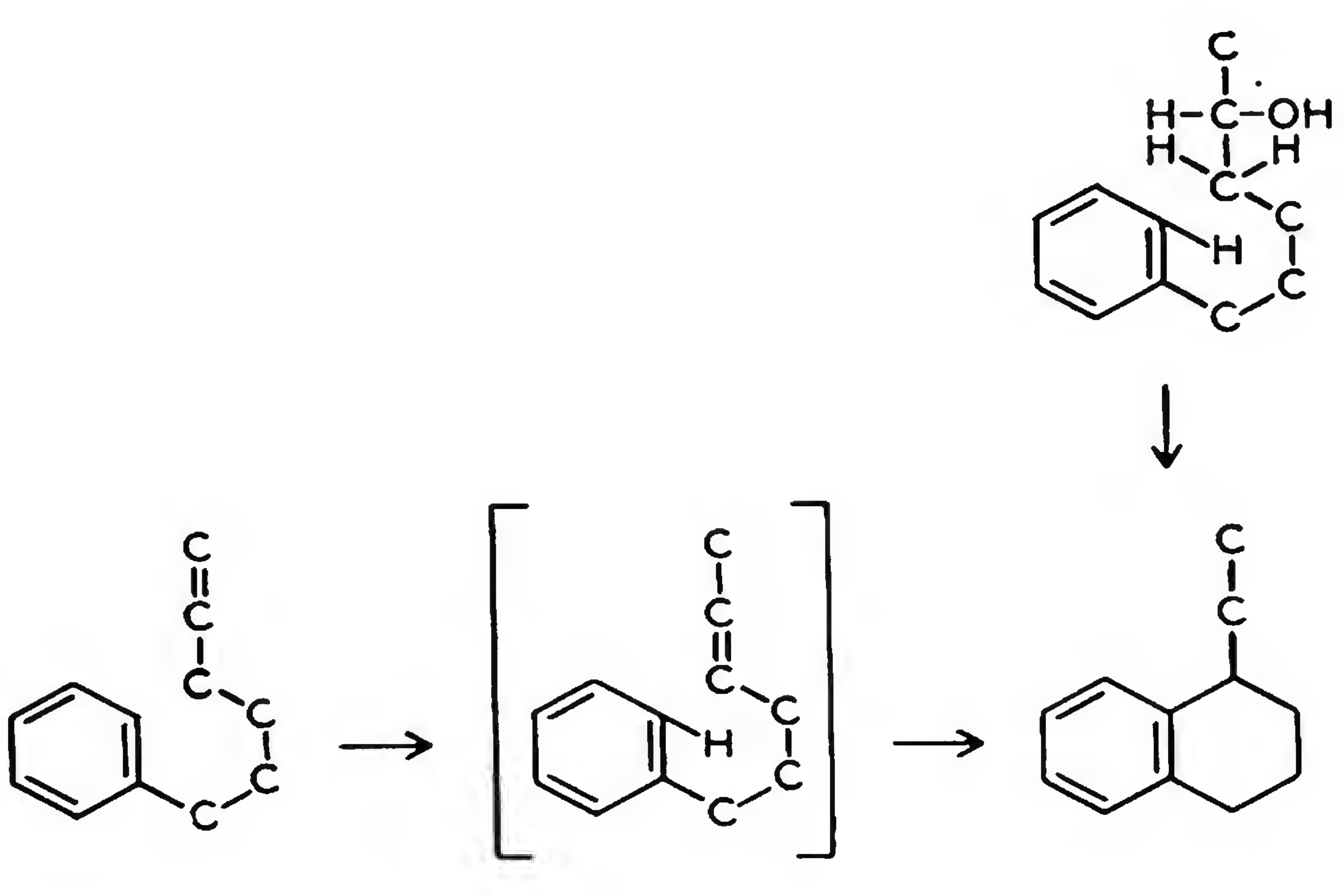


Studies [73] of the tetralin group have revealed that 1-methyltetralin can be obtained by cyclization of methylphenpropylcarbinol, 5-phenylpentene-1, ethylphenethylcarbinol, or 1-phenylpentene-2, using sulfuric acid. The action of 90-per cent sulfuric acid on 5-phenylpentene-1 gave

1-methyltetralin.[471] The isomerization of 1-phenylpentene-2 involves both cyclization and the migration of the double bond in a side-chain. Passage of 5-phenylpentene-1 (with carbon dioxide) over chromia at 250° yielded 1-phenylpentene-1, indicating a tendency toward conjugation of the ring and side-chain double bonds.[346a] In another instance, 1-phenylpentene-1 resulted when 1-phenylpentene-2 was heated at 150° with alcoholic potash.[309] It should be observed that here too the transfer of the labile hydrogen atoms is selective under the opposing roles assignable to acid and alkali:



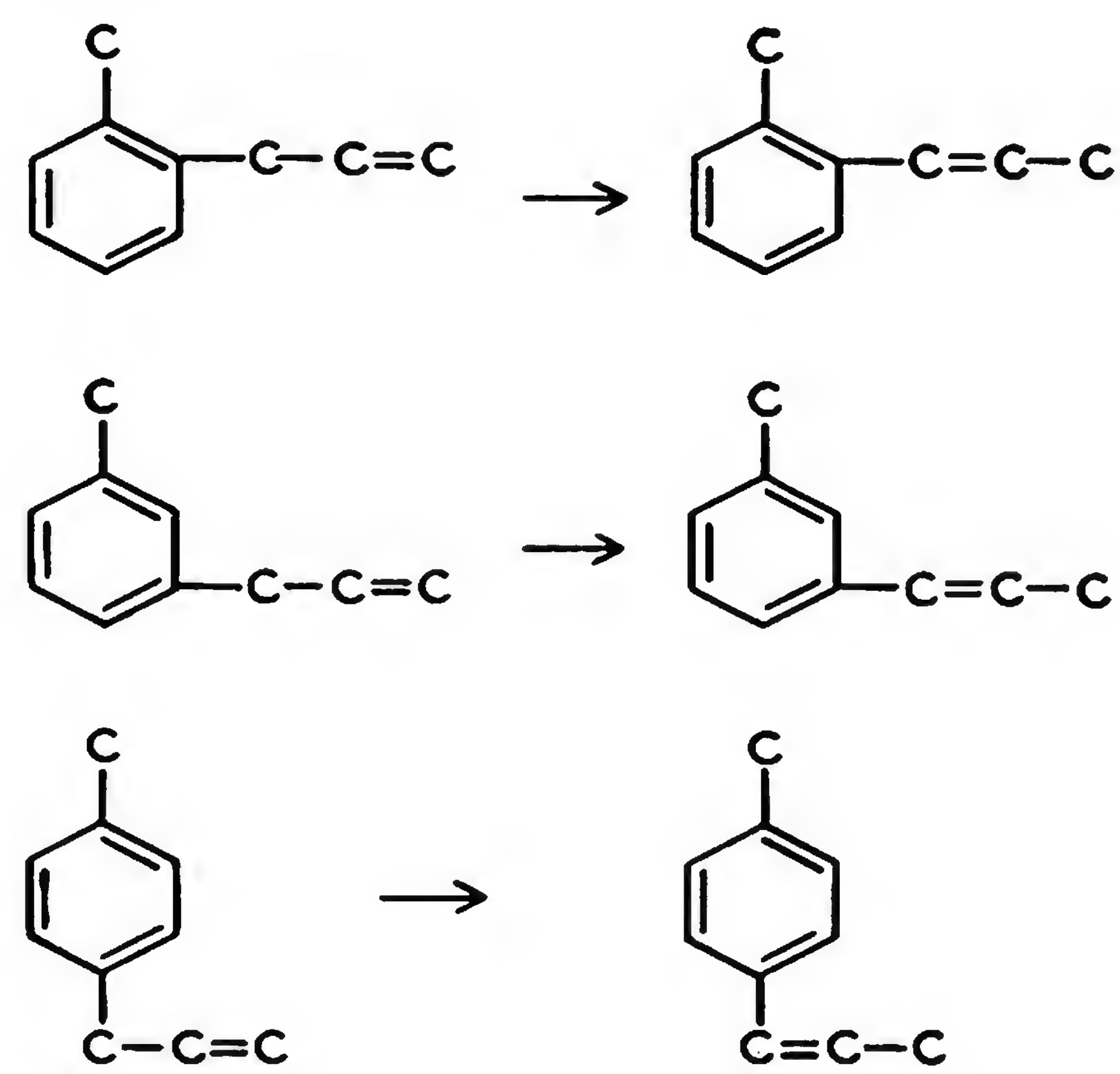
Similarly 1-ethyltetralin was prepared by the cyclization of either methylphenbutylcarbinol or 6-phenylhexene-1.[73] In the latter case, a shift in the location of the double bond is required, corresponding to the formation of either 6-phenylhexene-2 or 6-phenylhexene-3:



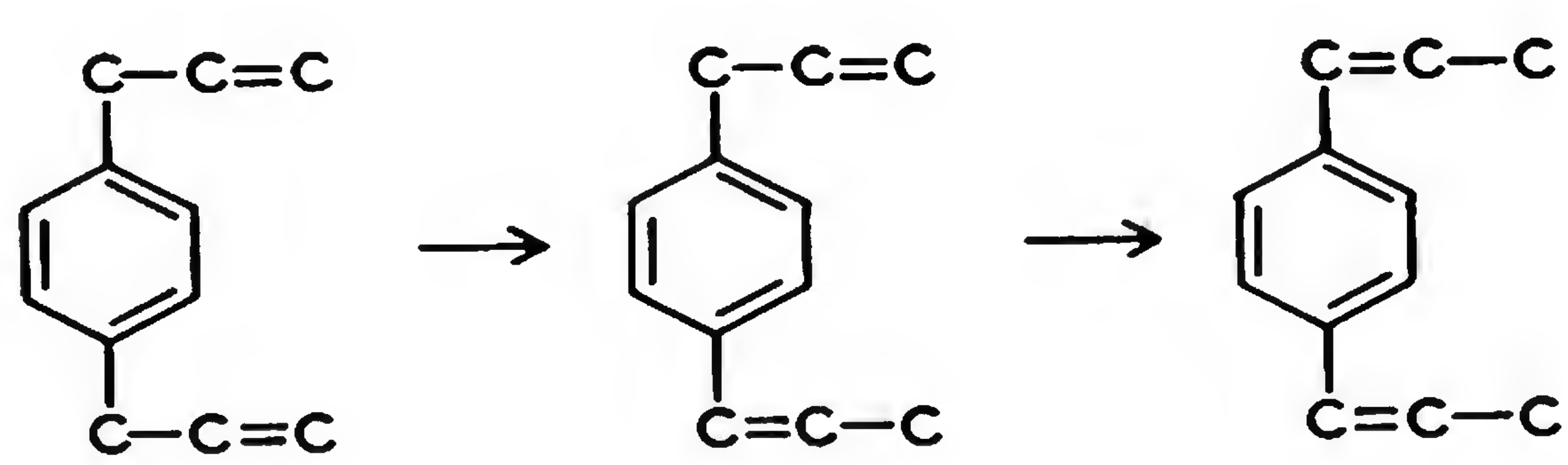
1-Ethyltetralin, for example, was prepared by the action of 90-per cent sulfuric acid on 6-phenylhexene-1.[471]

o-, *m*-, and *p*-Allyltoluenes, passed with carbon dioxide over alumina at 220-225°, were converted quantitatively into the corresponding *o*-, *m*-,

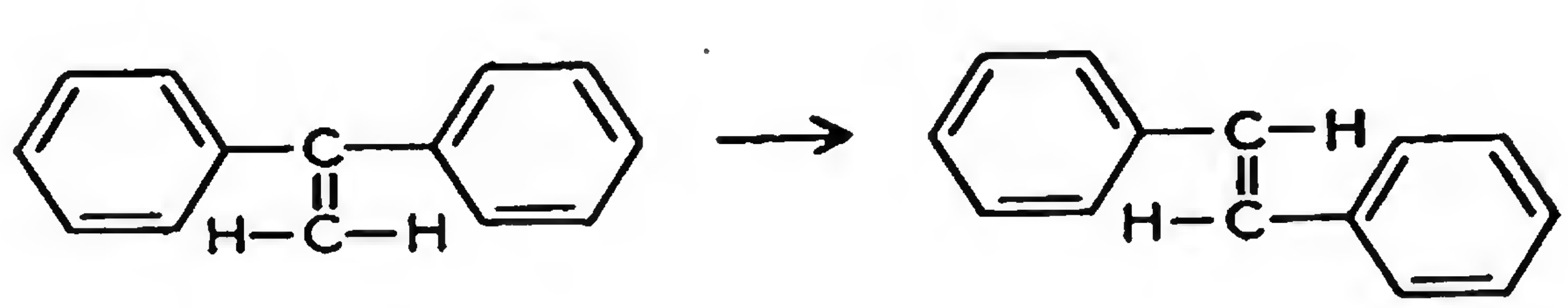
and *p*-propenyltoluenes.[338] *p*-Allyltoluene, passed with carbon dioxide over platinum (30 per cent) on charcoal at 300°, was converted into 84 per cent of *p*-propenyltoluene.[345] These isomerizations are illustrated by the following equations:



p-Diallylbenzene formed a mixture of *p*-allylpropenylbenzene and *p*-dipropenylbenzene when slowly conducted over alumina at 300° in the presence of carbon dioxide.[342a] These isomerizations probably proceed in two steps:

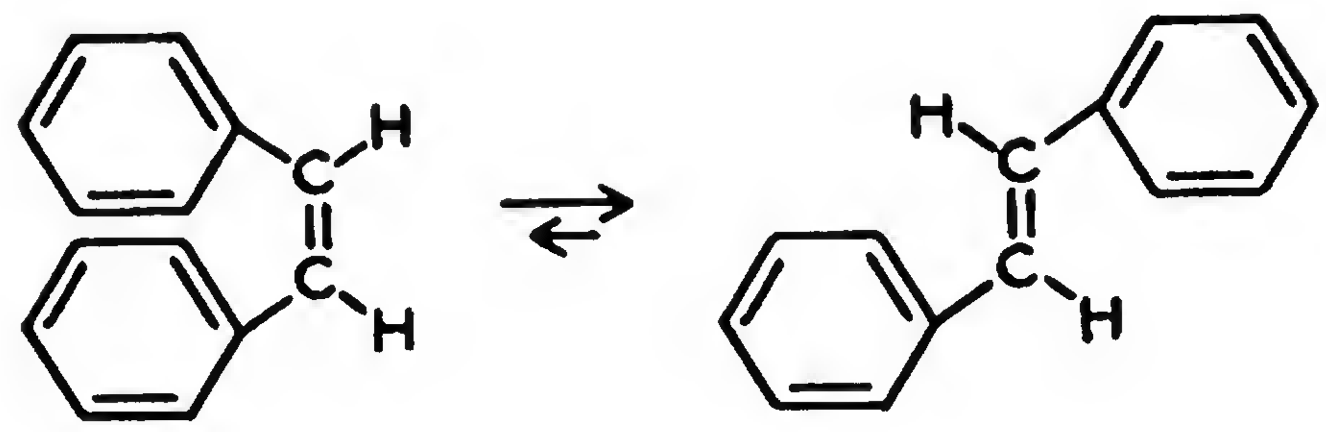


1,1-Diphenylethylene, when passed 2 or 3 times over infusorial-earth briquettes at 500°, was converted into *trans*-1,2-diphenylethylene (*i.e.*, stilbene):[456]



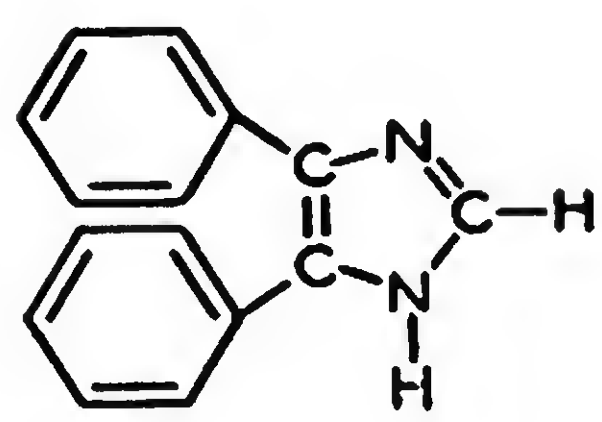
In the case of isomerizations in the 1,2-diphenylethylenes, there occurs a typical *cis-trans* conversion.[306, 567] It is a noteworthy fact that the ultraviolet absorption spectrum of *cis*-1,2-diphenylethylene (*i.e.*, isostilbene) resembles that of 4,5-diphenylglyoxaline, whereas that of the *trans*-form resembles 2-phenylindene:[645]

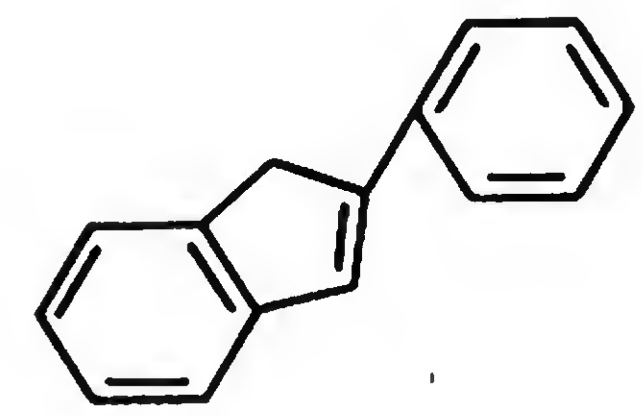
[Isostilbene]



[Stilbene]

Isostilbene resembles spectroscopically 4,5-diphenylglyoxaline





Stilbene resembles spectroscopically 2-phenylindene

The thermal isomerizations of vaporized *cis*-1,2-diphenylethylene (*i.e.*, isostilbene) and of the *trans* form (stilbene) at 320-341° were found to be reversible and unimolecular.[306] The activation energy amounted to 43 kilocalories per gram-mole. The equilibrium composition (starting with pure stilbene) is 7 per cent *cis* and 93 per cent *trans* form. These values may be erroneous, since the corresponding calibration curve [306] for the fusion of stilbene-isostilbene mixtures had an impossible curvature.[578]

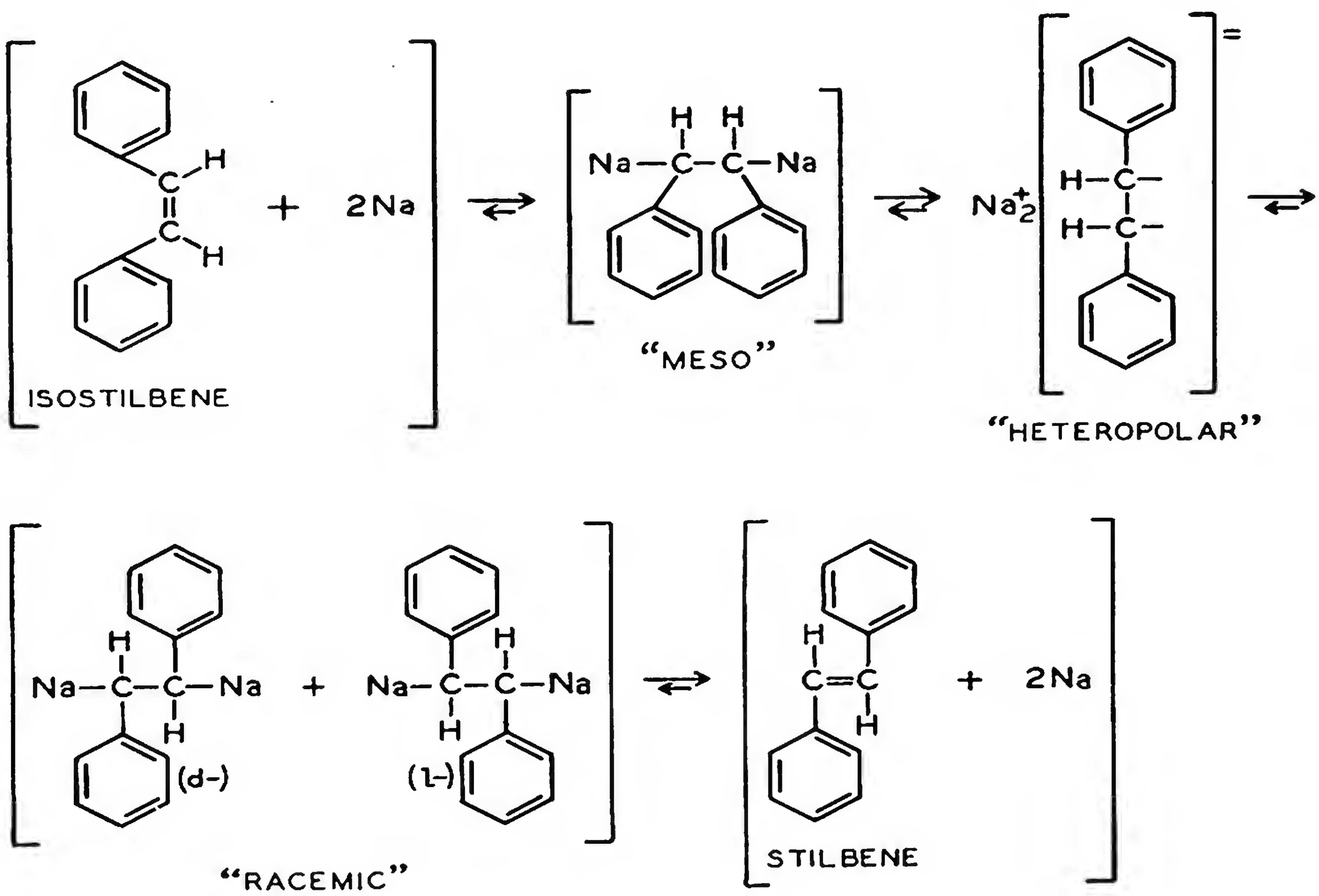
Exposure of hexane solutions of stilbene to ultraviolet light (3130Å) resulted in the formation of isostilbene with "100 per cent" quantum efficiency.[556] Similarly, isostilbene was obtained after the exposure of a benzene solution to ultraviolet light for 8 days.[567] Recent work [350a] indicates that the exposure of an "iso-octane" solution of stilbene to ultraviolet light (2537Å) is attended by an isomerization of 35 per cent of the excited molecules to isostilbene. The remaining, excited stilbene molecules return to their original state by undergoing fluorescence (48 per cent) or by exchanging their excess electronic energy for rotational and vibrational energies (17 per cent).

Isostilbene has been converted into stilbene by heat, sunlight, ultraviolet light, certain elements, boron fluoride,[447] and various acids. The *thermal* conversion of isostilbene into stilbene has been investigated at temperatures around 170°,[567, 572] 277°,[652] and 320°.[306] The isomerization of isostilbene by sunlight [428a, 572, 652] is accelerated remarkably by a trace of iodine.[572, 652] Exposure to sunlight of a carbon disulfide solution of isostilbene containing a trace of bromine gave stilbene.[567] Irradiation of an "iso-octane" solution of isostilbene by ultraviolet light (2537Å) was followed by the formation of 29 per cent of stilbene, and the reformation of 68 per cent of isostilbene, from the electronically excited molecules.[350a] Treatments of ethereal isostilbene solutions with lithium or sodium gave colored addition compounds, which were decomposed subsequently by carbon dioxide and alcohol, respectively.[516] These metalations-demetalations gave stilbene, but the yields were not reported.

Traces of stilbene-disodium or of stilbene-dilithium, in the complete absence of free alkali-metals, changed isostilbene instantly into stilbene with strong evolution of heat.[680] The discovery of the last reaction led to the theory that the organoalkali compounds dissociate readily in the following manner:[680]

$$>\underset{\displaystyle Na}{\underset{|}{C}}-\underset{\displaystyle Na}{\underset{|}{C}}< + C_6H_5CH{=}CHC_6H_5 \rightleftarrows >C{=}C< + C_6H_5\underset{\displaystyle Na}{\underset{|}{CH}}-\underset{\displaystyle Na}{\underset{|}{CH}}C_6H_5$$

The stilbene-dialkali compounds, moreover, were stated to have probably 3 tautomeric forms: a spatially undefined pure-heteropolar tautomer, a racemic (*dl*) form, and a meso form. The heteropolar tautomer is a form common to the racemic and meso forms. The last two forms, upon demetalation, would lead to stilbene and isostilbene, respectively; hence the catalysis by the dialkali compounds can be formulated as the following right shift of reactions, which illustrates the postulated sodium-ion transfers.



Random addition of one sodium atom at a time to the ethylene linkage has been advanced to explain carboxylation and methylation of 1,2-diphenylethylene.[655]

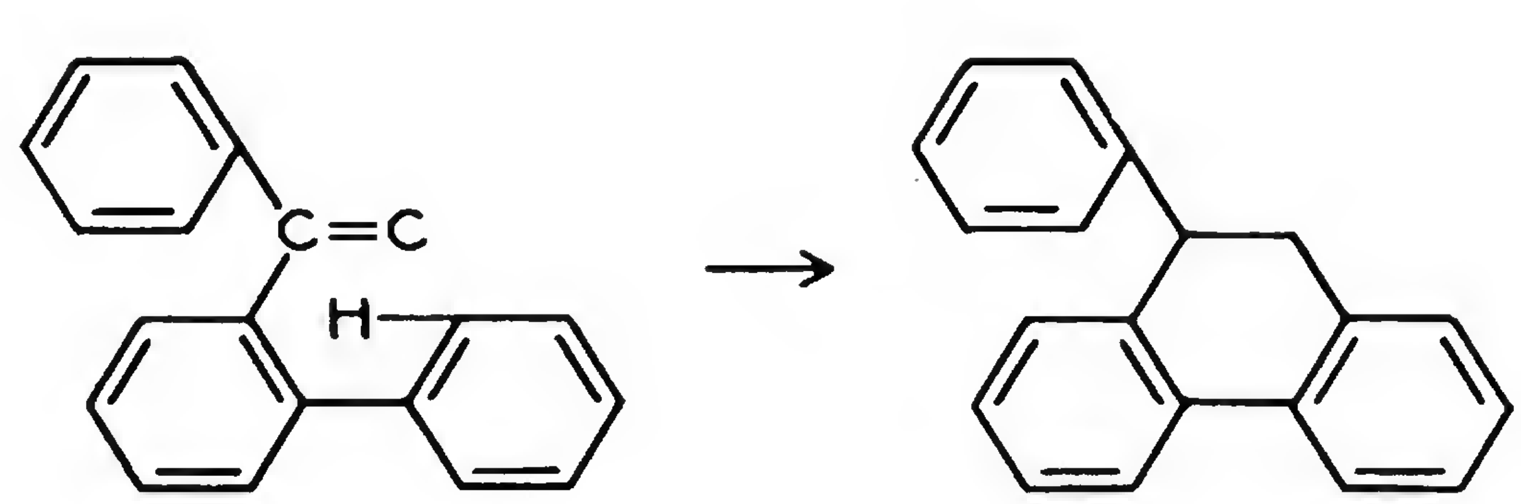
Isostilbene was converted into stilbene by treatment with hydrogen bromide when aided by any of the following agents: heat,[608] artificial light,[303] sunlight,[303] reduced copper or iron,[608] reduced nickel,[607, 608] palladium or platinum blacks,[608] air,[608] oxygen,[607] ascaridole,[303] or benzoyl peroxide.[303, 607] Some work indicates that hydrogen bromide plus air does not readily isomerize isostilbene in benzene solution in the dark.[303]

Catechol, hydroquinone, ethyl mercaptan, and thiophenol are effective inhibitors in the isomerization of isostilbene by hydrogen halides.[303] Isostilbene "boiled" with 20-per cent hydrochloric acid gave stilbene;[570] hydrogen chloride was ineffective at room temperature in the presence of either ascaridole or benzoyl peroxide.[303] Exposure of isostilbene to vapors of fuming nitric acid gave stilbene;[300, 567, 572] this method is reminiscent of the isomerization of oleic into elaidic acid. From these experiments, it follows that several interpretations may be given to the reactivity of alkenes and their catalysts. For instance, it is claimed that isomerization induced by hydrogen bromide is due to oxidation into bromine,[303] to an excitation of hydrogen bromide,[607, 609] or to the paramagnetic behavior of bromine atoms which enables them to interact with the double bond.[324] In several cases, however, purely thermal isomerization appears to be an adequate explanation.

Recently, benzoic acid was used as a catalyst for the liquid-phase reactions between isostilbene and stilbene at 200° in an atmosphere of nitrogen.[578] Starting from either isomer, the same equilibrium mixture, 4 per cent isostilbene and 96 per cent stilbene, was obtained. The heat of activation of isostilbene at 214-223° was found to be 36.7 kilocalories per gram-mole. An oxygen atmosphere, used in place of nitrogen and benzoic acid, led to the formation of an organic-acid product that converted isostilbene into stilbene.[578] Addition of hydrogen chloride to a nitrogen atmosphere was sufficient "to convert isostilbene into stilbene in 4 hours at 190°."[578]

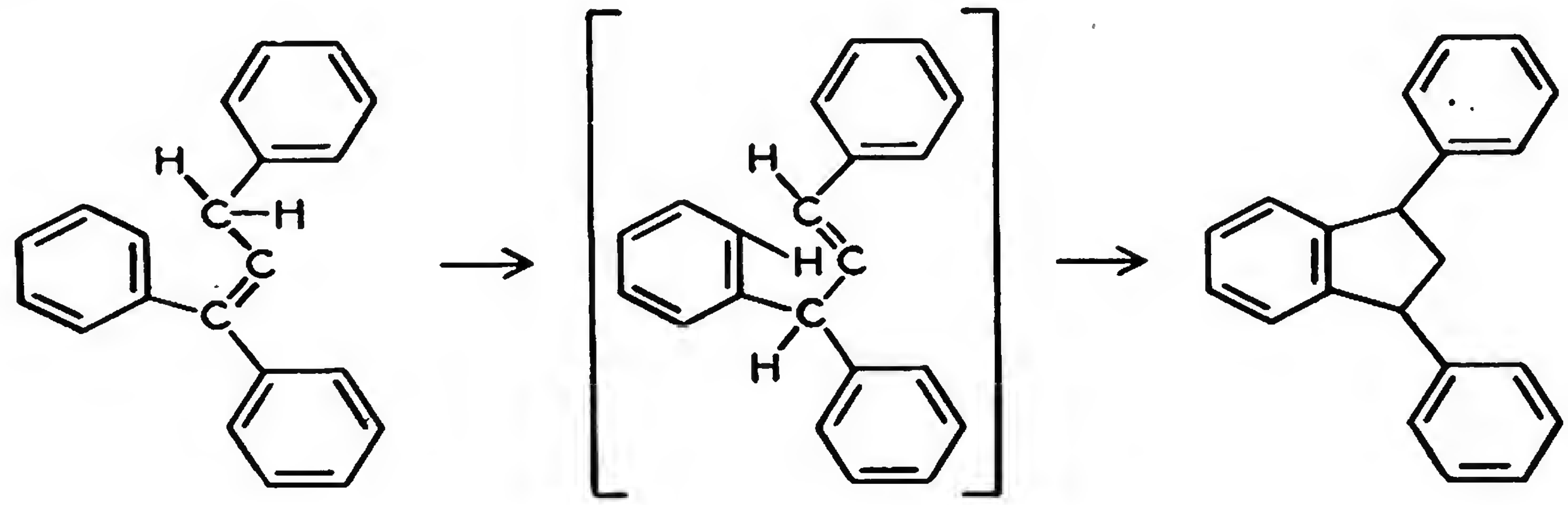
It is the opinion of the authors that the mechanism of isostilbene-stilbene isomerization parallels that of *cis*- and *trans*-butene-2. These transformations, therefore, should be investigated by means of parallel studies. It may be pointed out that the conditions (heat and/or presence of boron fluoride, oxidizing agents, or acids) reported as favorable for the conversion of isostilbene into stilbene are those of energy addition or the presence of catalysts having electron-deficient natures. These two factors enable the double bond to be opened temporarily by movement of electrons.

o-Phenyl-1,1-diphenylethylene was cyclized by phosphorus pentachloride into 9-phenyl-9,10-dihydrophenanthrene:[50]

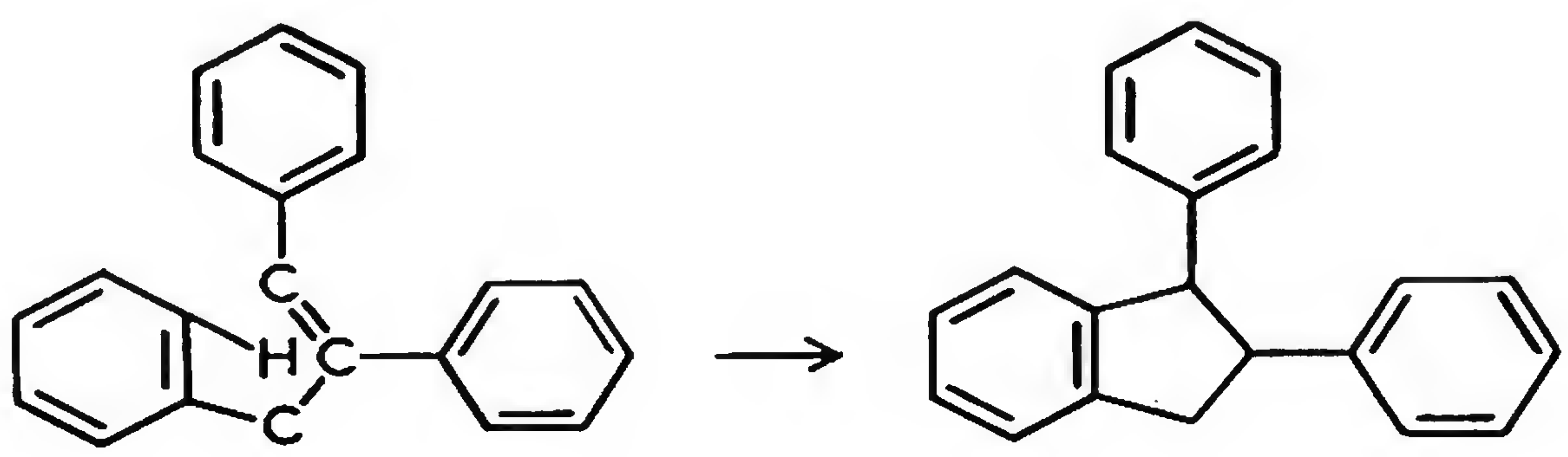


1,1,3-Triphenylpropene-1, when treated for 8 days with concentrated sulfuric acid, gave 16 per cent of 1,3-diphenylindane.[517] A 10 per cent

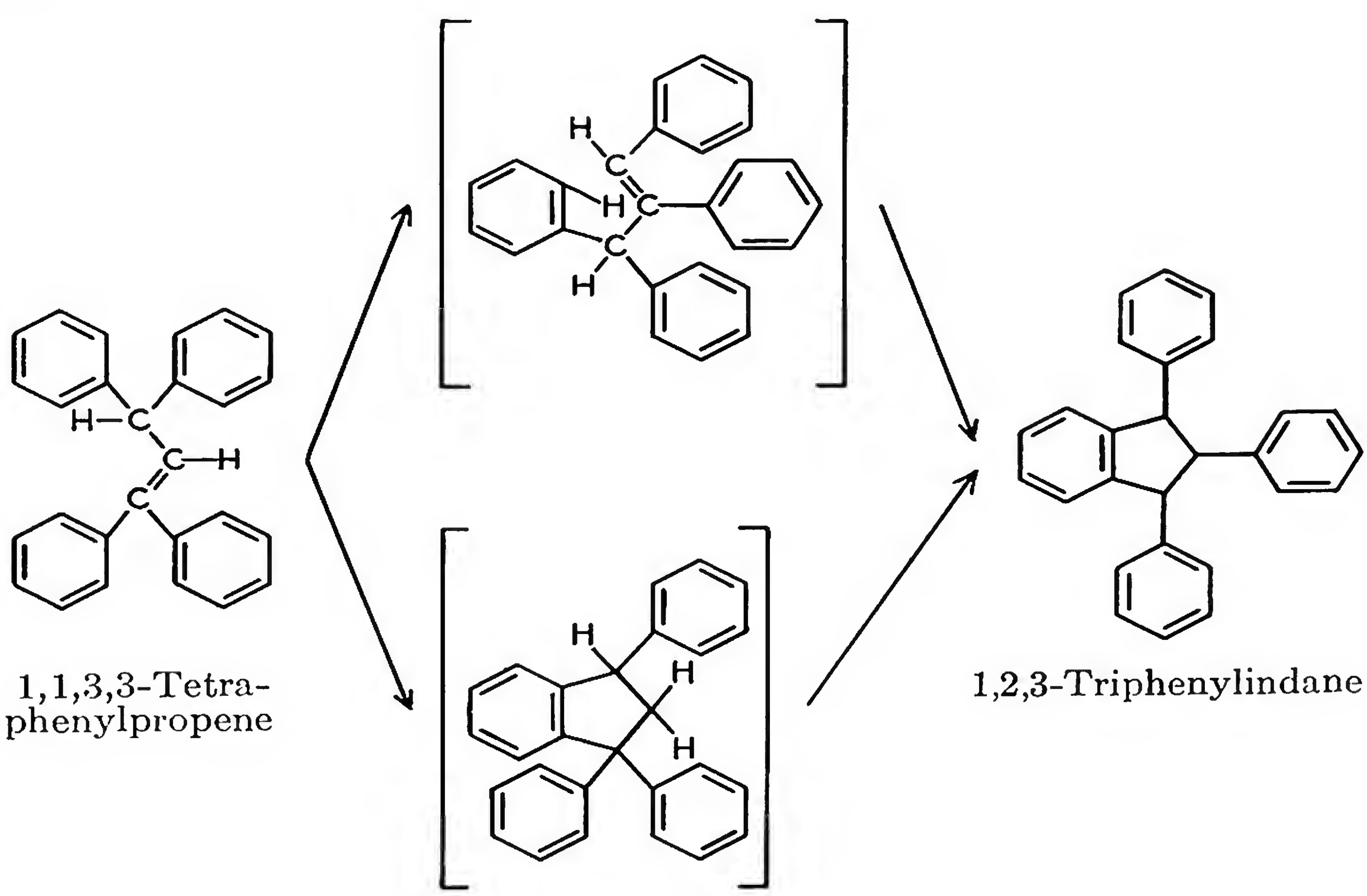
yield of 1,3-diphenylindane resulted when diphenylbromomethane acted in ether upon the organolithium compound of 1,1,3-triphenylpropene-1.[518] These isomerizations can be explained as a transient conversion into 1,3,3-triphenylpropene-1 (*i.e.*, 1,1,3-triphenylpropene-2), followed by cyclization:[517]



1,2,3-Triphenylpropene probably can be isomerized to 1,2-diphenylindane:[52]



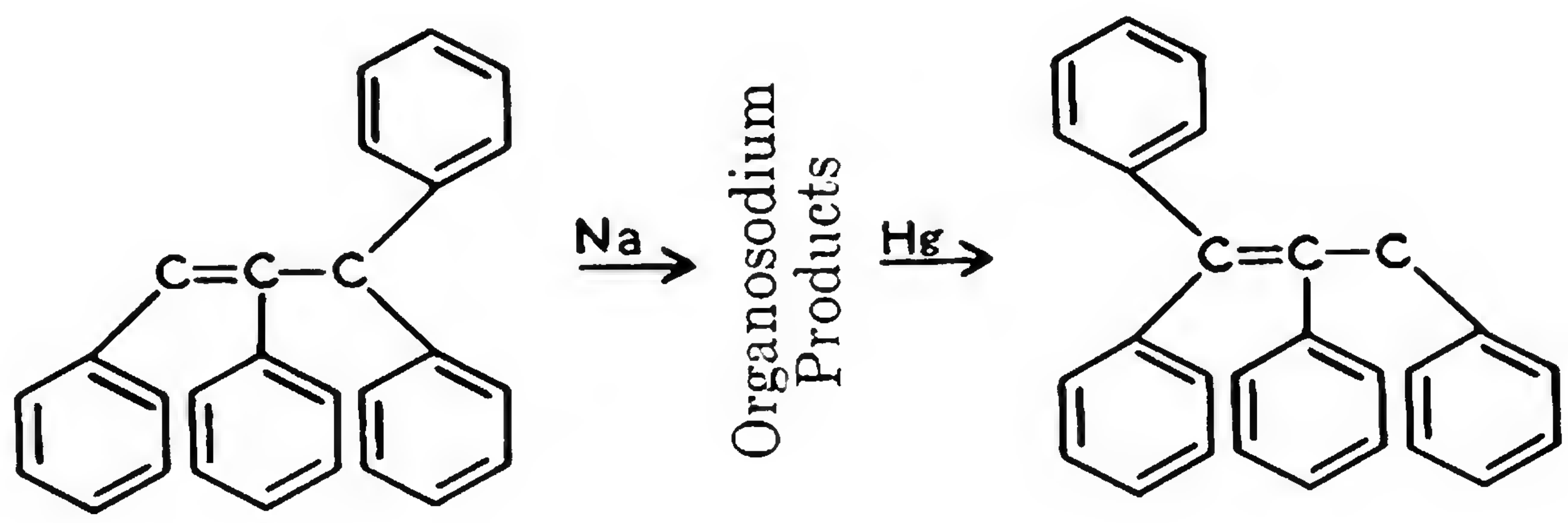
1,1,3,3-Tetraphenylpropene, when dissolved in ether and shaken for 8 days with lithium, formed a soluble lithium derivative which was hydrolyzed later by alcohol into 1,2,3-triphenylindane.[516] The reaction has not been explained. The following equations are proposed by the authors:



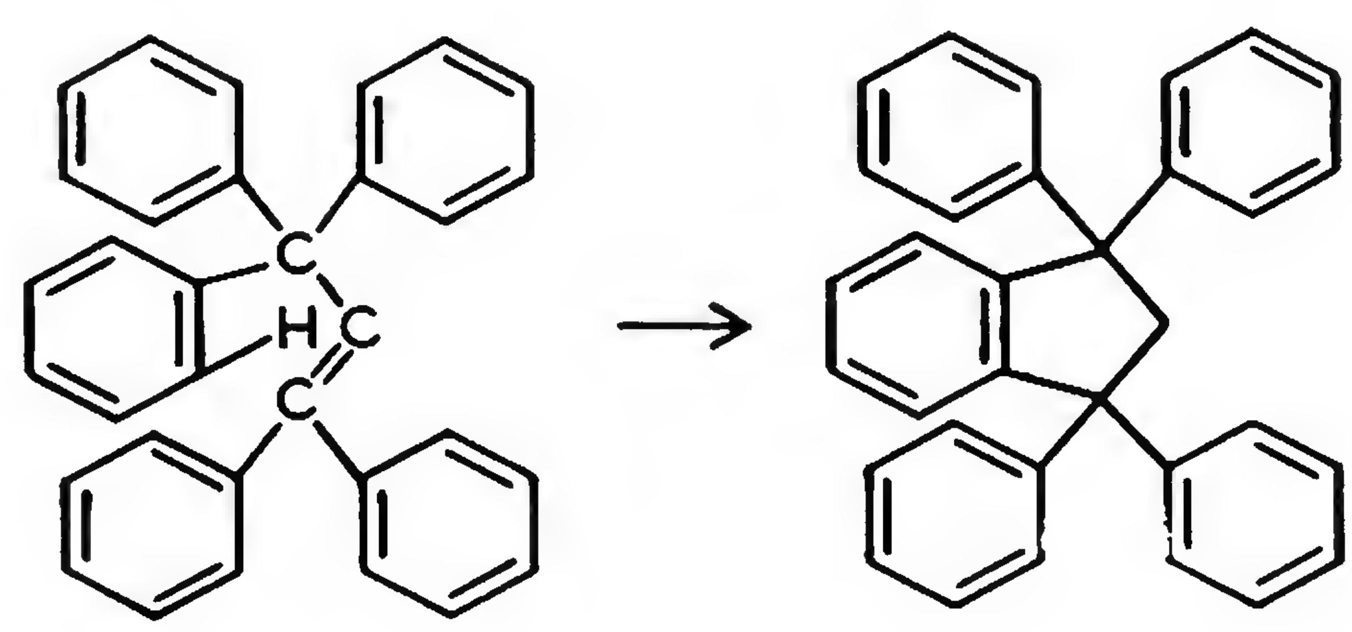
1,1,3,3-Tetraphenylpropene

1,2,3-Triphenylindane

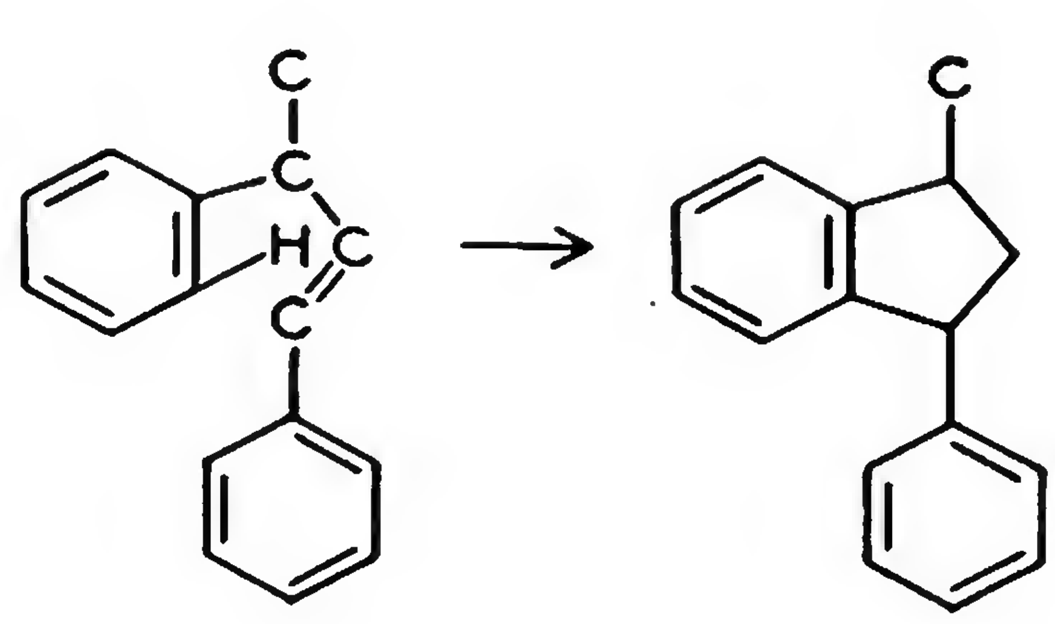
1,2,3,3-Tetraphenylpropene-1 (*i.e.*, 1,2-diphenyl-1-benzhydrylethylene, m.p. 131°) was isomerized to 1,1,2,3-tetraphenylpropene-1 (*i.e.*, 1,1,2-triphenyl-2-benzylethylene, m.p. 142°) by conversion into organosodium products by means of sodium metal, followed by a demetalation in the presence of mercury.[53] A considerable amount of 1,1,2,3,4,5,6,6-octaphenylhexadiene-1,5 occurs in this reaction as a by-product, due to a Würtz-type condensation.



1,1,3,3,3-Pentaphenylpropene was isomerized to 1,1,3,3-tetraphenylindane when boiled with a 4 per cent solution of sulfuric acid in acetic acid:[316]



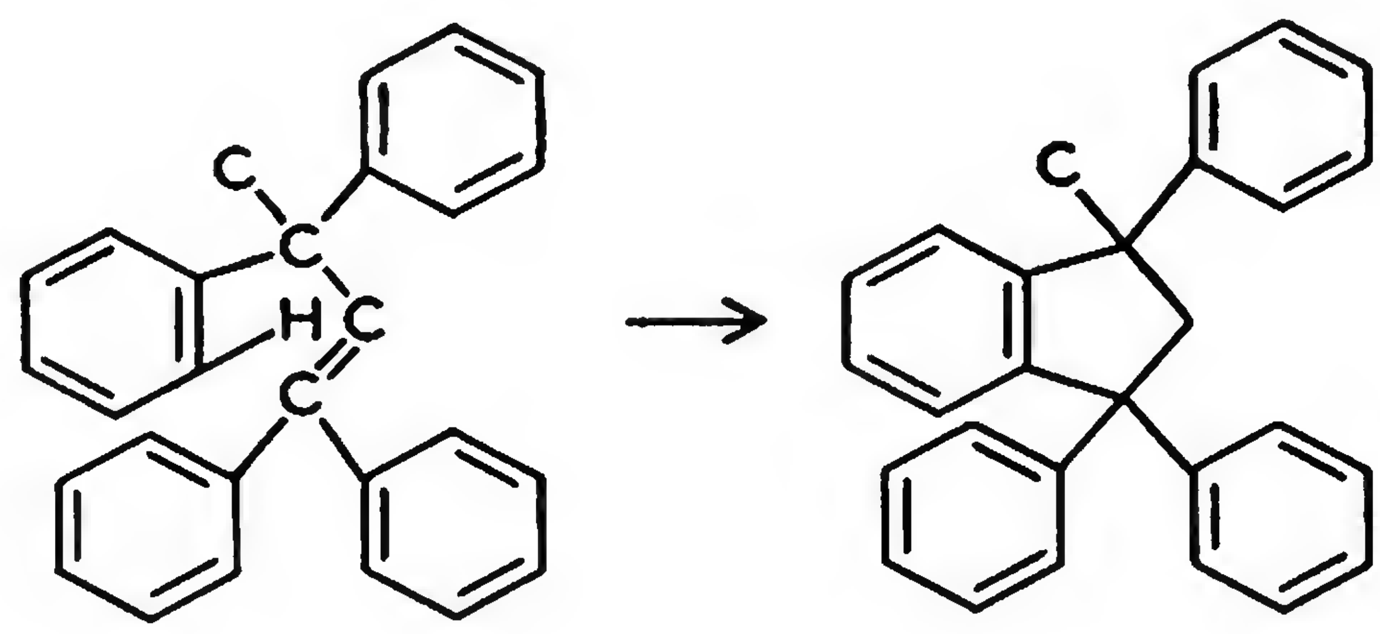
1,3-Diphenylbutene-1, which is termed "liquid distyrene" in the literature, is believed to undergo a very slow isomerization in the presence of traces of sulfuric acid.[569] The product was reported to be 1,3-diphenylbutene-2,[569] but it is probably 1-methyl-3-phenylindane.[468] The last hydrocarbon was produced by heating 1,3-diphenylbutene-1 for 40 hours under reflux with dilute sulfuric acid:[468]



2,3-Diphenylbutene-2 occurs in a "stable" α-form (m.p. 65-66°) and an "unstable" β-form (m.p. 104°). These are stated to be an exception to the general rule: "the most stable geometrical isomer has the higher

melting point."[458] The β-form, when heated for a few minutes with sulfuric acid-treated pumice, and then distilled *in vacuo,* gave irreversibly over 5 per cent of the α-form.[458]

1,1,3,3-Tetraphenylbutene cyclized at 215° in the presence of "Floridin" into 1-methyl-1,3,3-triphenylindane.[332] The product[332] was taken erroneously to be 1,1,3,3-tetraphenylcyclobutane.[54, 522] 1,1,3,3-Tetraphenylbutene was converted also into the indane by treatment with concentrated sulfuric acid,[54] stannic chloride plus benzene partly saturated with dry hydrogen chloride,[522] dimethylsulfate,[43a] and probably by iodine in a slow cyclization at 100°.[54] The isomerization is obviously an "internal alkylation" of a 3-phenyl group at its ortho position:



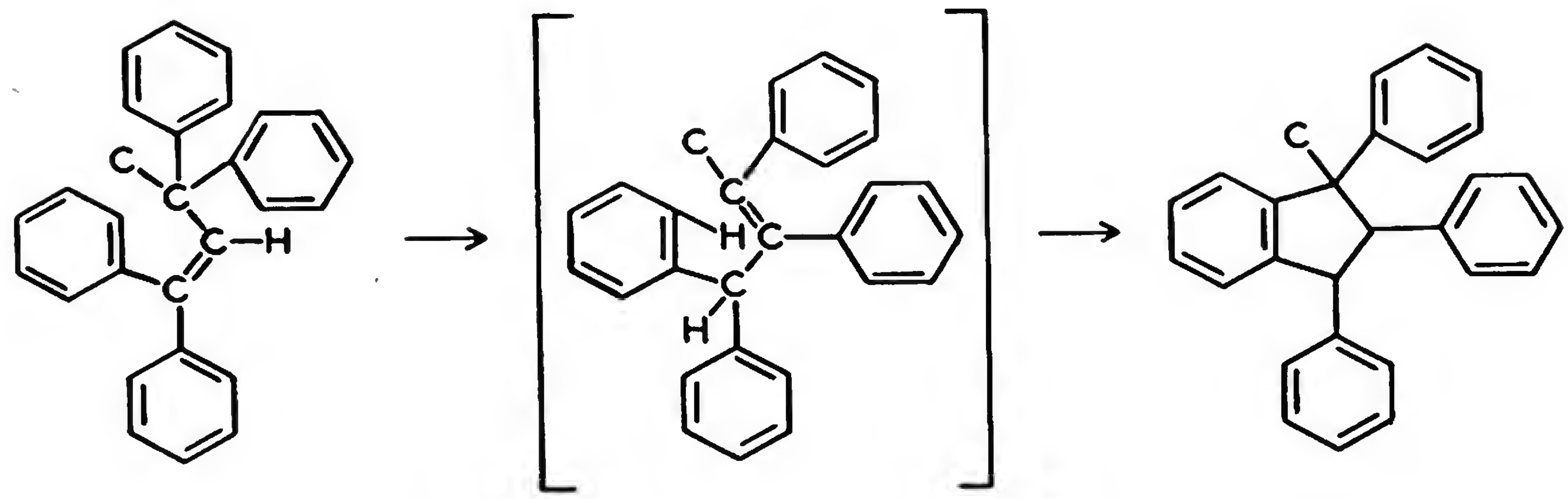
The isomerizations of 1,1,3,3-tetraphenylbutene into 1,1,4,4-tetraphenylbutene-2 and 1-methyl-1,2,3-triphenylindane, which result when the organolithium compound of the first hydrocarbon is hydrolyzed by alcohol, were explained as follows:[55]

$$2(C_6H_5)_2C{=}CH{-}C(C_6H_5)_2{-}CH_3 + 2Li \longrightarrow \begin{array}{l} \quad\quad\;\; Li \\ (C_6H_5)_2C{-}CH{-}C(C_6H_5)_2{-}CH_3 \\ (C_6H_5)_2C{-}CH{-}C(C_6H_5)_2{-}CH_3 \\ \quad\quad\;\; Li \end{array}$$

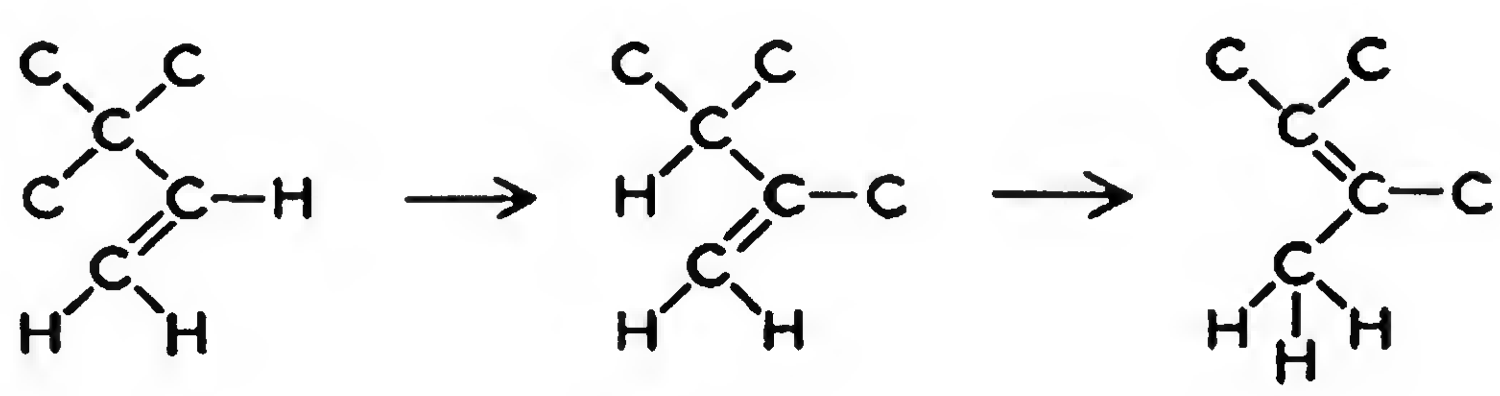
$$\big\downarrow C_2H_5OH$$

$$\left(\begin{array}{l} (C_6H_5)_2CH{-}CH_3 \\ (C_6H_5)_2C{=}CH_2 \\ (C_6H_5)_2CH{-}CH{=}CH{-}CH(C_6H_5)_2 \end{array}\right)$$

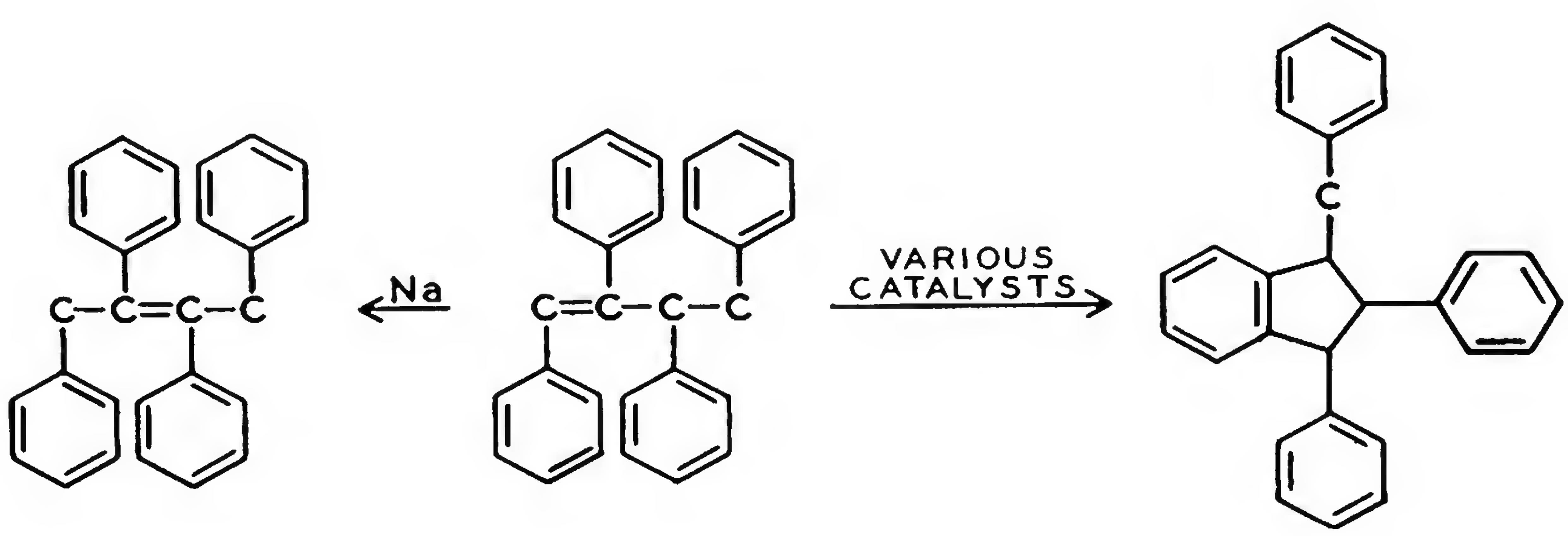
The formation of 1-methyl-1,2,3-triphenylindane was stated (without further explanation) to result from the migration of a phenyl group. This product requires the isomerization of 1-methyl-1,3,3-triphenylindane (the expected product), or that of 1,1,3,3-tetraphenylbutene into 1,2,3,3-tetraphenylbutene or 1,1,2,3-tetraphenylbutene-2. The interpretation of the reaction as the conversion of 1-methyl-1,3,3-triphenylindane finds support in the known isomerizations of aryl indenes, whereas the postulated cyclization of 1,1,2,3-tetraphenylbutene-2:



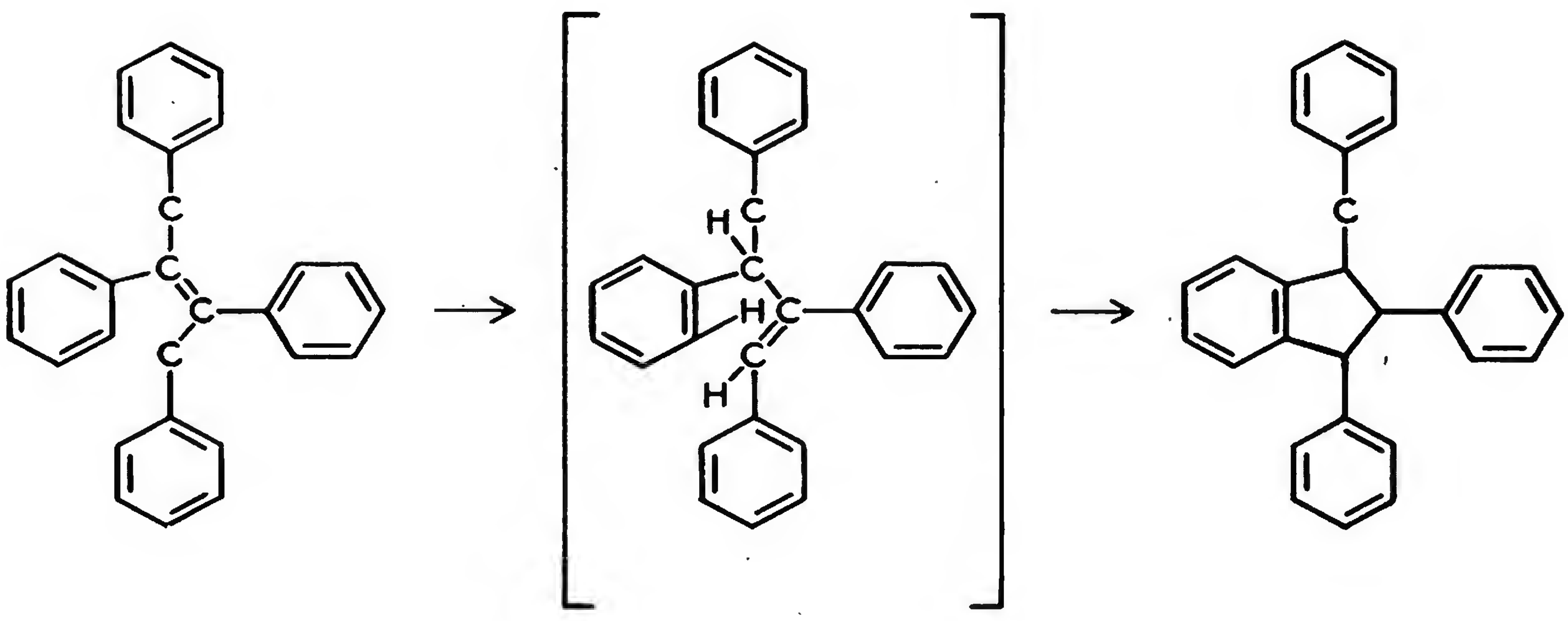
corresponds to the "right-shift" of reactions shown by 3,3-dimethylbutene:



1,2,3,4-Tetraphenylbutene-1 occurs in a geometrical form of m.p. 96° and a more reactive form of m.p. 150°.[57] The treatment of the less reactive form (in ether) with sodium, and then with alcohol, led to the formation of 1,2,3,4-tetraphenylbutene-2 with m.p. 80°. The other form, when treated in the same manner, cyclized into 1-benzyl-2,3-diphenylindane and isomerized only slightly into 1,2,3,4-tetraphenylbutene-2. The same cyclization ensued in experiments on the more reactive form using: (a) sodium in boiling amyl alcohol, (b) stannic chloride plus hydrogen chloride-saturated benzene, or (c) red phosphorus, concentrated hydriodic acid, plus acetic acid under reflux:

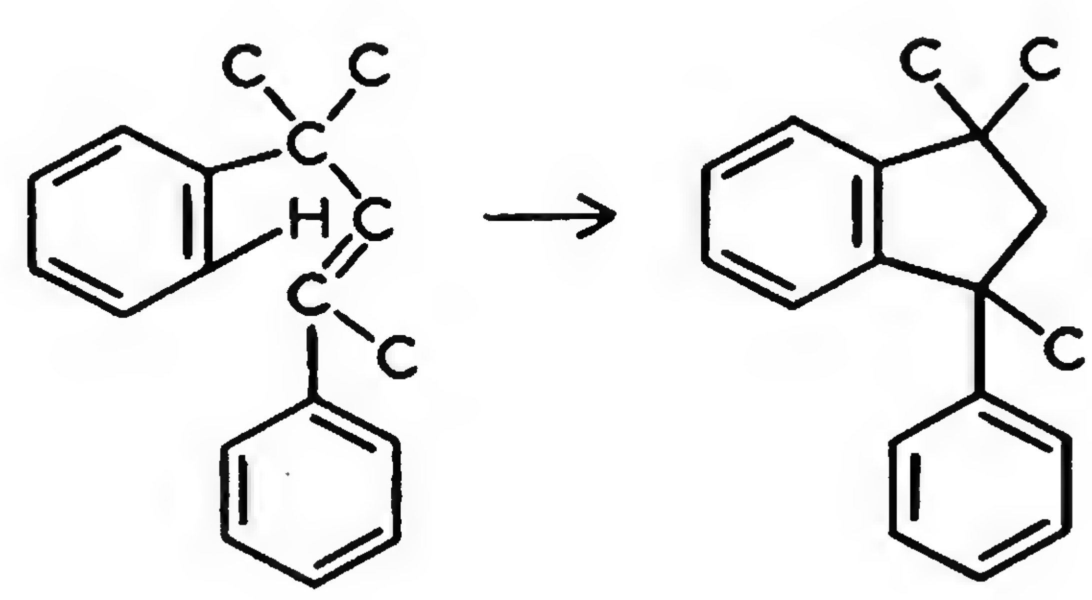


1,2,3,4-Tetraphenylbutene-2 (melting point 80°) was converted into 1-benzyl-2,3-diphenylindane upon high-vacuum distillation or by treatment in ether with sodium followed by alcohol.[57] The investigators assumed that a preliminary conversion into 1,2,3,4-tetraphenylbutene-1 occurs in the treatment with sodium:



This proposal, and the *cis-trans* orientations of aryl groups about the double bond of these butenes, remain to be investigated.

2,4-Diphenyl-4-methylpentene-2, when treated with aluminum chloride plus benzene for 2 days, or with stannic chloride for 20 hours, gave respectively 20 and 40 per cent of 1,1,3-trimethyl-3-phenylindane: [51]



Isomerizations of the alkenyl benzenes are given in Table 36, p. 366.

Conclusions

1. Isomerizations of alkenyl benzenes by shift of the double bond within the unsaturated side-chain occur under the influence of heat; these isomerizations are aided by catalysts, such as alcoholic potash, alumina, chromia, palladium, platinum, nickel-on-asbestos, and infusorial earth.

2. The resulting isomers are formed by a stepwise migration of the side-chain double bond toward the ring (eventually, conjugation with the ring double bonds).

3. Cyclizations of alkenyl benzenes occur under the influence of strong acids, such as phosphoric and sulfuric acids, and miscellaneous catalysts ("Floridin," iodine (?), lithium, sodium, aluminum chloride, stannic chloride, and phosphorus pentachloride).

4. The catalytic activity of "Floridin," iodine, aluminum chloride, stannic chloride, and phosphorus pentachloride may be attributed to the presence of acids. These acids are those (a) used in the initial activation of the "Floridin," (b) produced by the action of iodine on hydrocarbons (liberating hydrogen iodide), and (c) formed by hydrogenation-

hydrolysis (*e.g.*, hydrogenolysis) of the aluminum chloride, stannic chloride, or phosphorus pentachloride (liberating hydrogen chloride). The activity of lithium and sodium may be due to the formation of "lithium hydride" and "sodium hydride," respectively, since an isomerization with phenyl migration involves obviously a momentary loss of labile hydrogens.

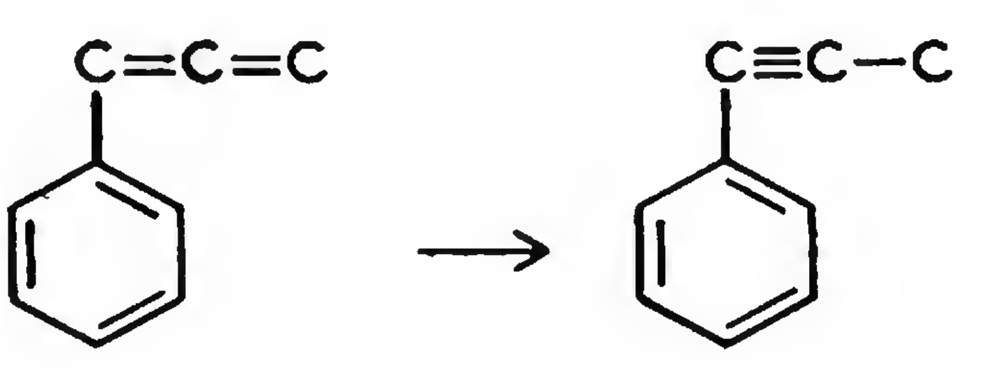
5. The typical *cis-trans* isomerization in the case of 1,2-diphenylethylene (stilbene and isostilbene) has been studied extensively. Thermally, it probably proceeds in a manner analogous to that of butene-2, by a transfer of hydrogen with the "opening and closing" of the double bond (via partial break and rotation, or by the formation of a new tetrahedron). Such a mechanism seems preferable to an interchange of a hydrogen atom and a phenyl group. In the case of the corresponding catalytic interconversions, it seems necessary to postulate the *cis*-meso-*heteropolar*-racemic-*trans* shifts.

Alkadienyl Benzenes

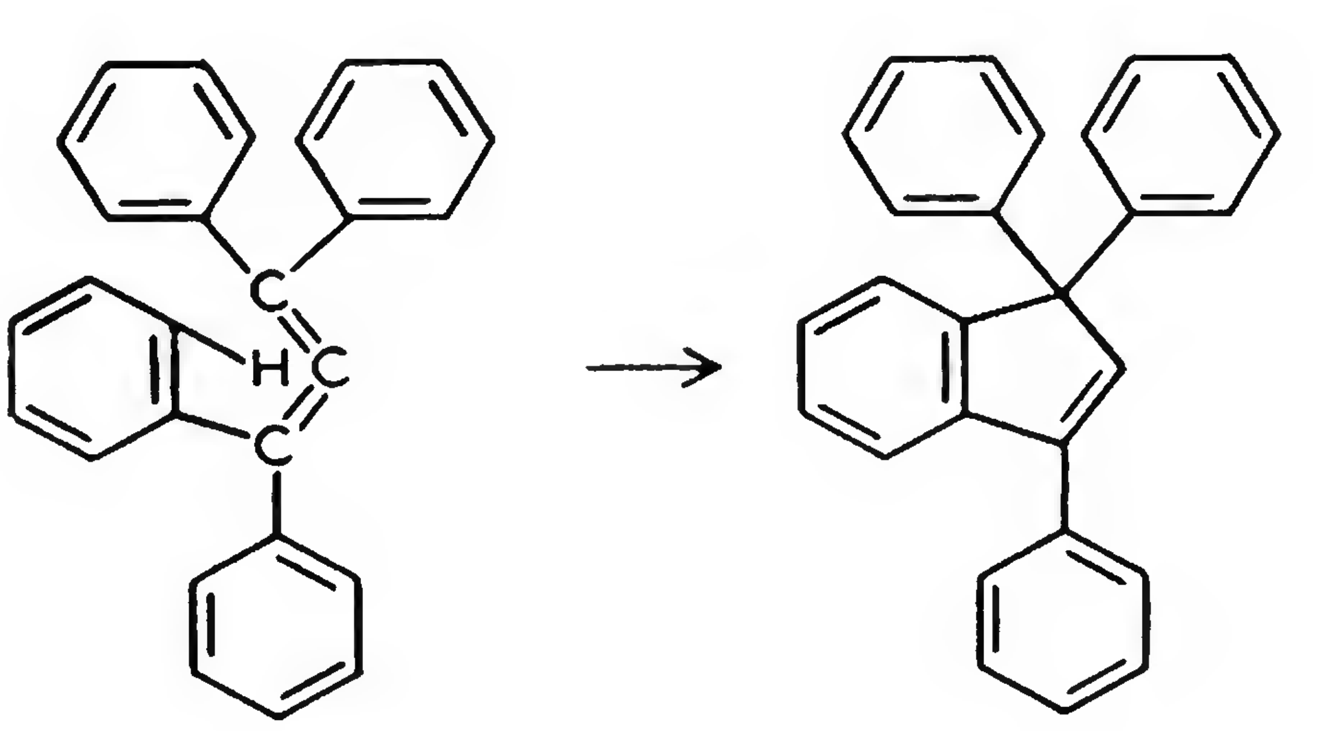
The alkadienyl benzenes are either allenic or non-allenic in structure. Side-chains in these hydrocarbons do not undergo an extensive interconversion of double bonds, in contrast to the behavior of the aliphatic alkadienes.

Allenic Alkadienyl Benzenes

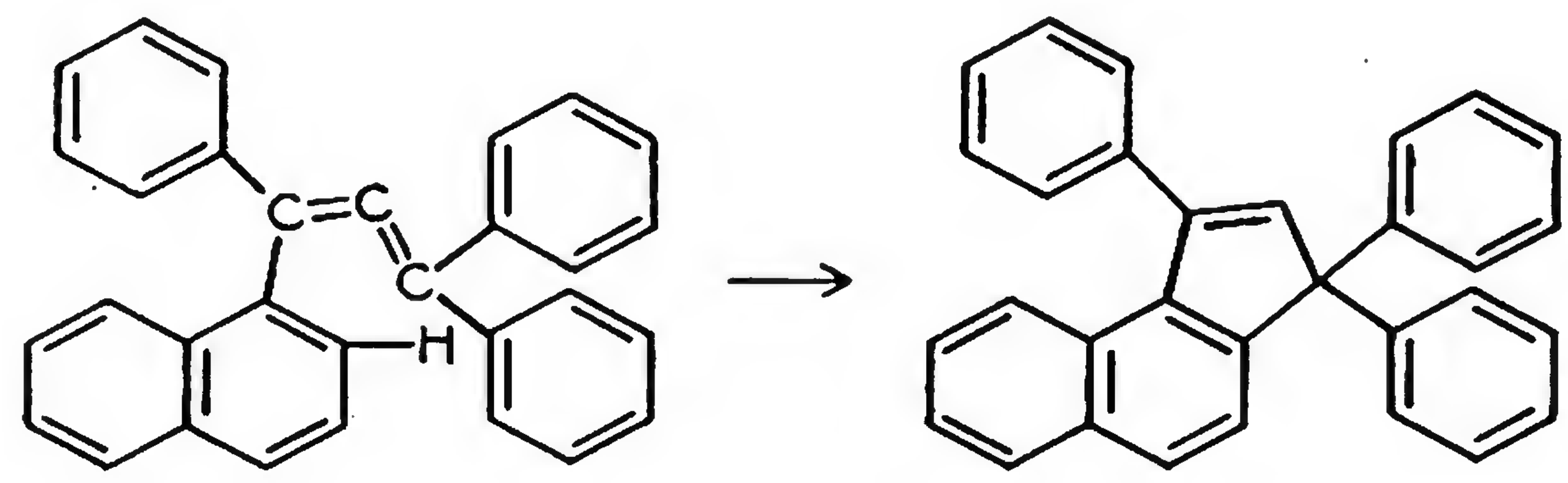
Phenylpropadiene (*i.e.*, phenylallene) isomerized to 1-phenylpropyne-1 under the action of alcoholic potash at 105-110° for 6.5 hours: [214]



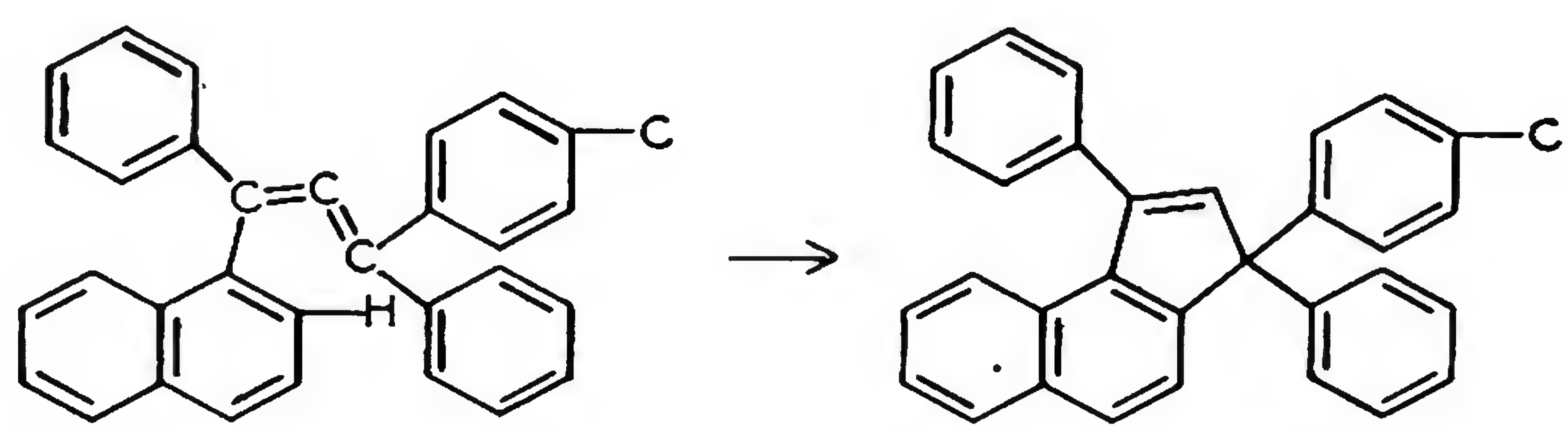
Tetraphenylpropadiene (*i.e.*, tetraphenylallene) was cyclized to 1,1,3-triphenylindene by treatment with: (a) iodine in benzene, (b) hydrogen bromide and hydrogen chloride as gases, or their saturated solutions in acetic acid, (c) boiling "concentrated" hydrochloric acid, or (d) boiling acetic acid.[613] Acetic acid, saturated with hydrogen chloride at the boiling point, is an effective catalyst.[317]



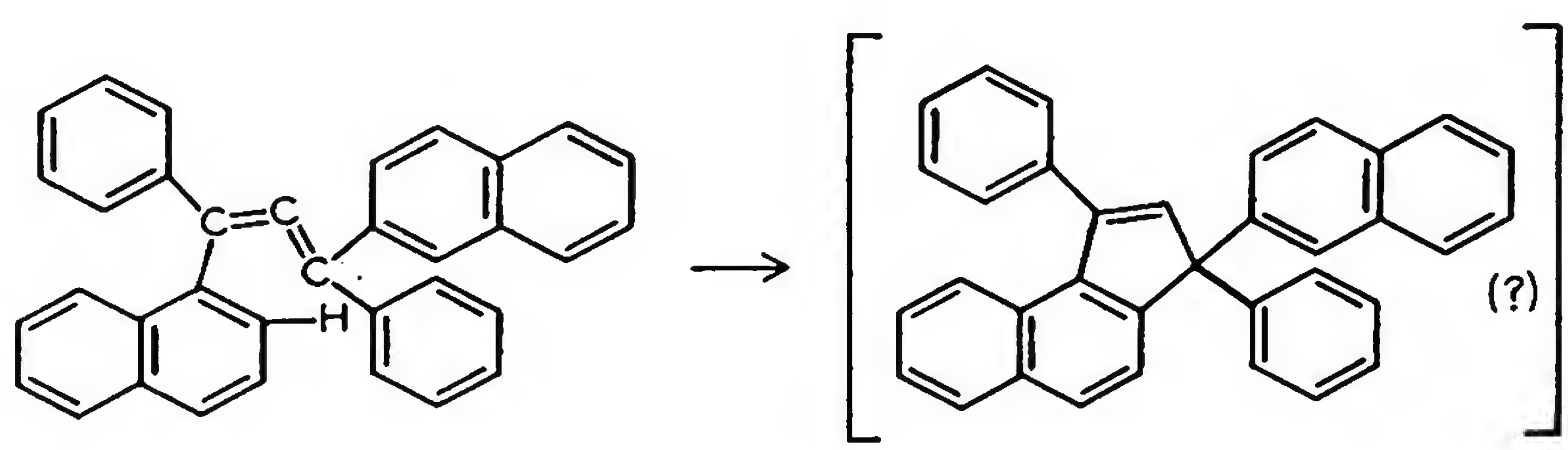
Triphenyl-(1-naphthyl)-propadiene, when heated under reflux with hydrogen chloride in acetic acid, or with *p*-toluenesulfonic acid in benzene, formed 1,3,3-triphenyl-3-α-naphthindene (*i.e.*, 1,1,3-triphenyl-4:5-benzindene):[106]



1,3-Diphenyl-1-*p*-tolyl-3-(1-naphthyl) propadiene, treated with hydrogen chloride in acetic acid, was isomerized to 1,3-diphenyl-3-*p*-tolyl-3-α-naphthindene (*i.e.*, 1,3-diphenyl-1-*p*-tolyl-4:5-benzindene):[106]

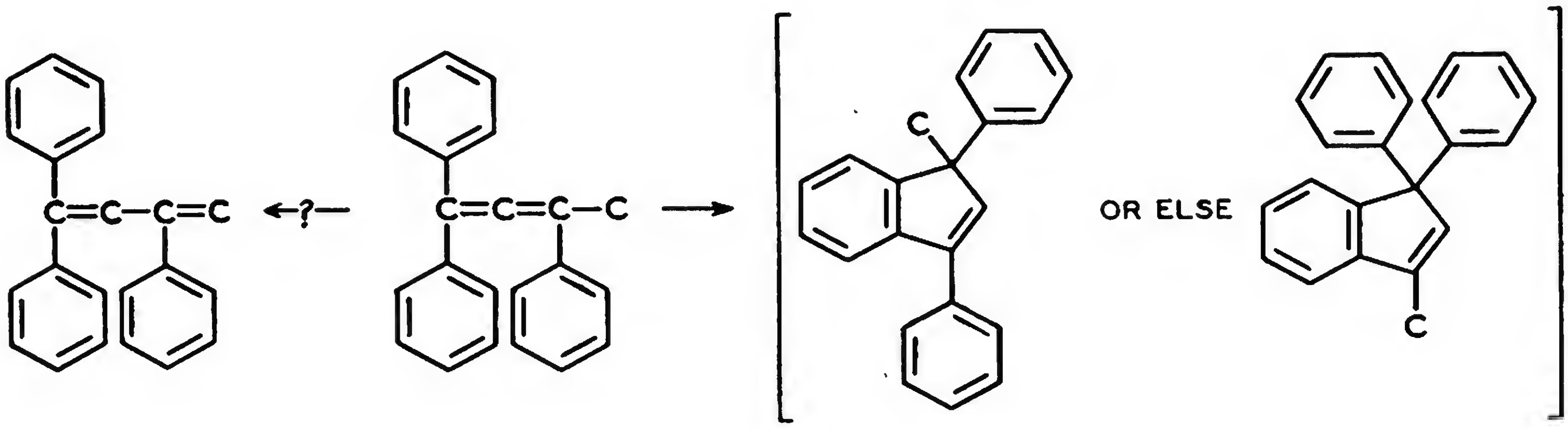


d-1,3-Diphenyl-1,3-di-(1-naphthyl) propadiene was racemized at the boiling point of decalin used as solvent.[358] The racemate, heated for 5 minutes with hydrogen chloride plus acetic acid, or for one hour with iodine in benzene, was cyclized to an isomer (m.p. 233-234°) taken to be 1,3-diphenyl-3-(1-naphthyl)-3-α-naphthindene (*i.e.*, 1,3-diphenyl-1-α-naphthyl-4:5-benzindene.[358] This assigned structure is tentative, since the formations of 1-phenyl-1,3-di-(1-naphthyl)indene and 1,3-diphenyl-1-(1-naphthyl) benzonaphthene (*i.e.*, 1,3-diphenyl-1-(1-naphthyl)-peri-naphthindene) were not excluded definitely:



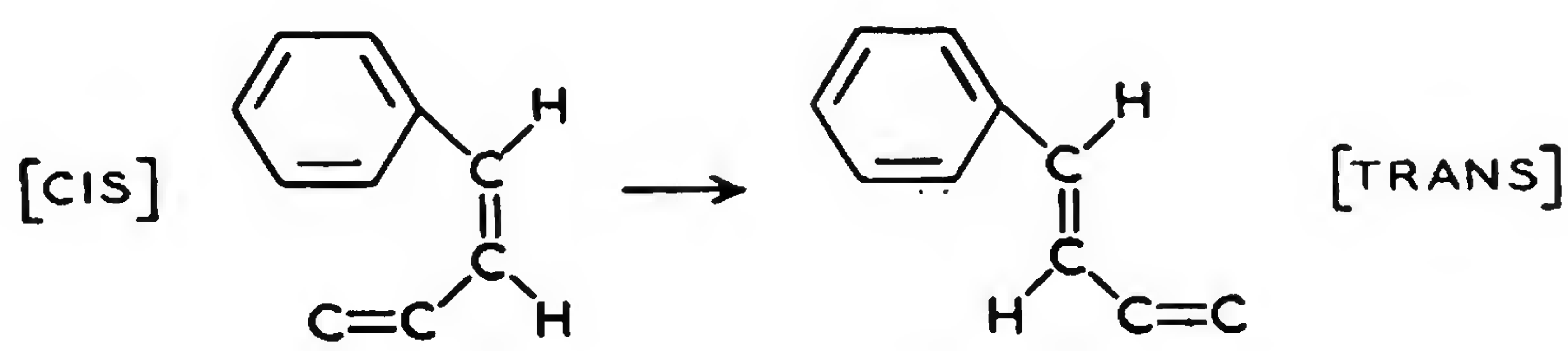
1,1,3-Triphenylbutadiene-1,2, treated with acetic acid plus sulfuric acid, gave a liquid product slowly crystallizing, in part, to a methyldiphenylindene (m.p. 56°).[679] Theoretically, this cyclization product can be expected to contain 1-methyl-1,3-diphenylindene and 1,1-diphenyl-3-methylindene. Boiling of 10 per cent solutions of 1,1,3-triphenylbuta-

diene-1,2 in acetic acid or acetic anhydride, gave an isomer of m.p. 163°, probably 1,1,3-triphenylbutadiene-1,3.[679]

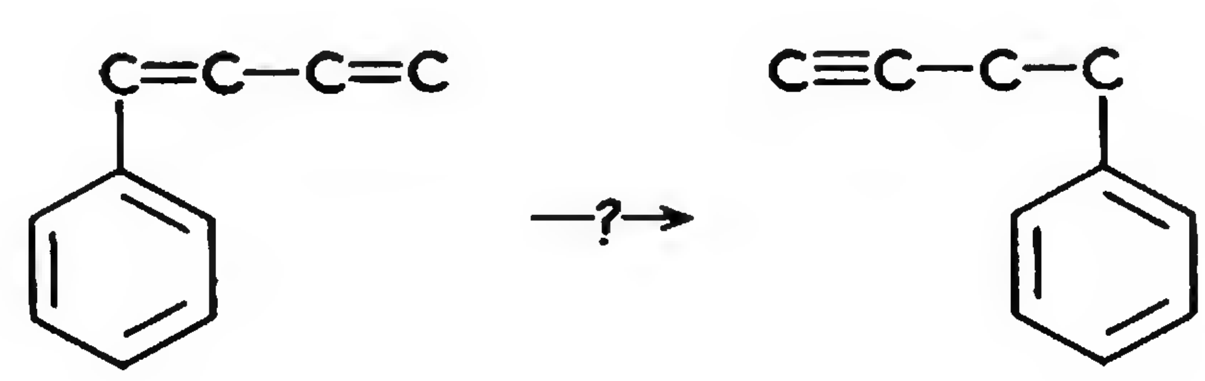


Non-Allenic Alkadienyl Benzenes

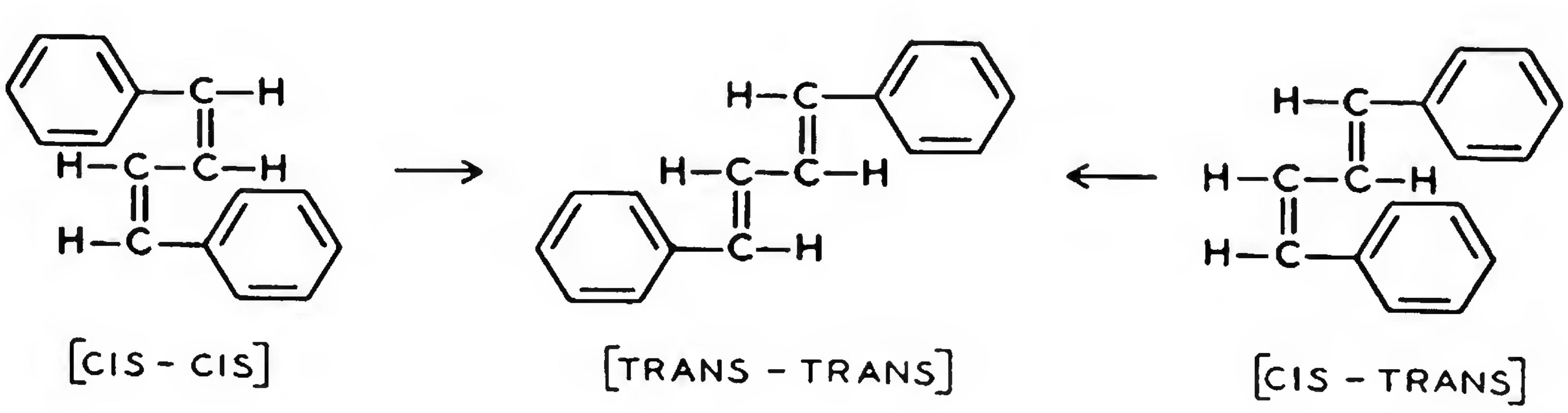
Cis-1-phenylbutadiene-1,3-isomerized completely into *trans*-1-phenylbutadiene-1,3 when allowed to stand overnight with a trace of hydrochloric acid, and then distilled: [395]



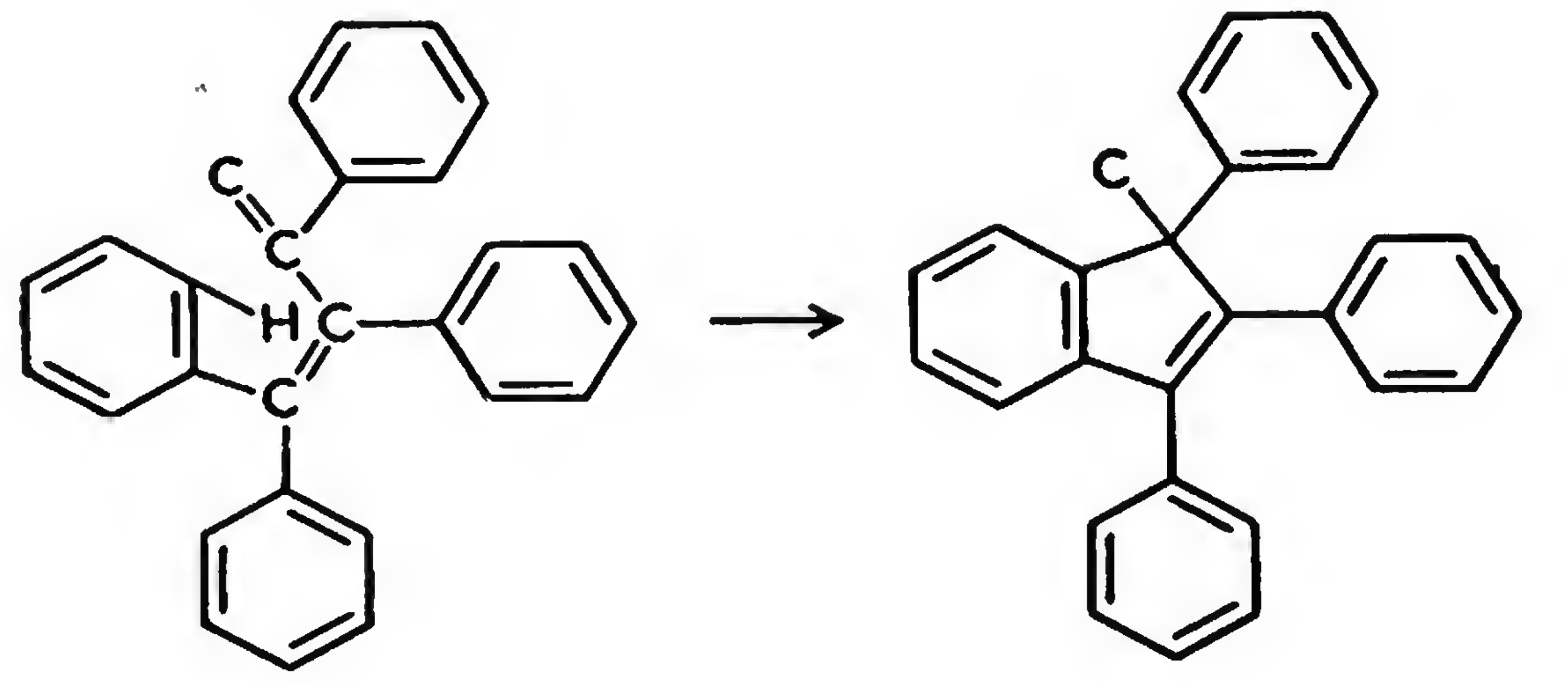
1-Phenylbutadiene-1,3, when passed over "Floridin" at 290-300°, gave probably 4-phenylbutyne-1, along with a large amount of polymer: [555]



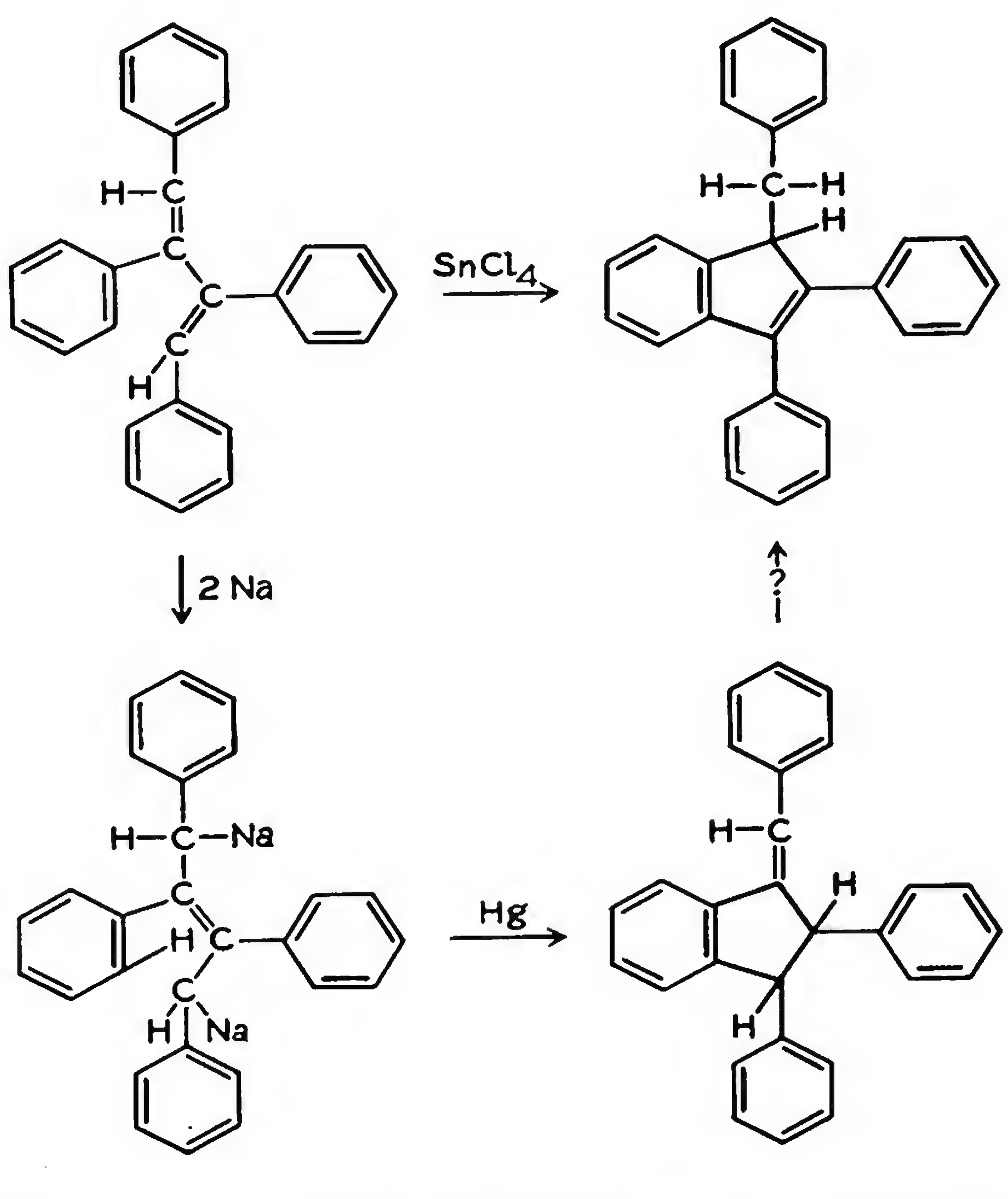
1,4-Diphenylbutadiene-1,3 is known in 3 geometrically isomeric forms: the stable *trans-trans* or α-form (m.p. 151°); the *cis-cis* or β-form (m.p. 70.5°), and the liquid *cis-trans* or γ-form.[572] The *cis-cis* and *cis-trans* forms isomerized into the stable *trans-trans* form upon exposure to sunlight: [572]



1,1,2,3-Tetraphenylbutadiene-1,3 yielded quantitatively 1-methyl-1,2,-3-triphenylindene under the action of boiling acetic acid, containing a little sulfuric acid, for 5 minutes: [316a]



1,2,3,4-Tetraphenylbutadiene-1,3 was 60 per cent isomerized to 1-benzyl-2,3-diphenylindene when treated in benzene with stannic chloride.[57] Treatment in ether with sodium (for 3 days), followed by mercury, resulted in another isomer, that of 1-benzylidene-2,3-diphenylindane, and in 1-benzyl-2,3-diphenylindane plus 1,2,3,4-tetraphenylbutane.* The accepted course of the metalation-demetalation is a 1,4-addition of sodium, followed by the formation of 1-benzylidene-2,3-diphenylindane in the presence of mercury:



* The isomerization to 1-benzyl-2,3-diphenylindene, via stannic chloride in benzene, warrants an investigation of the benzylideneindanes. The latter should be capable of conversion into benzylindenes in the presence of "acidic" catalysts.

The experimental data on isomerizations of alkadienyl benzenes are given in Table 37, p. 378.

Conclusions

1. The allenic alkadienyl benzenes have been isomerized into: an alkynyl benzene, a racemic allenic alkadienyl benzene, a probably non-allenic phenylated alkadiene, indenes, and several 3-α-naphthindenes.

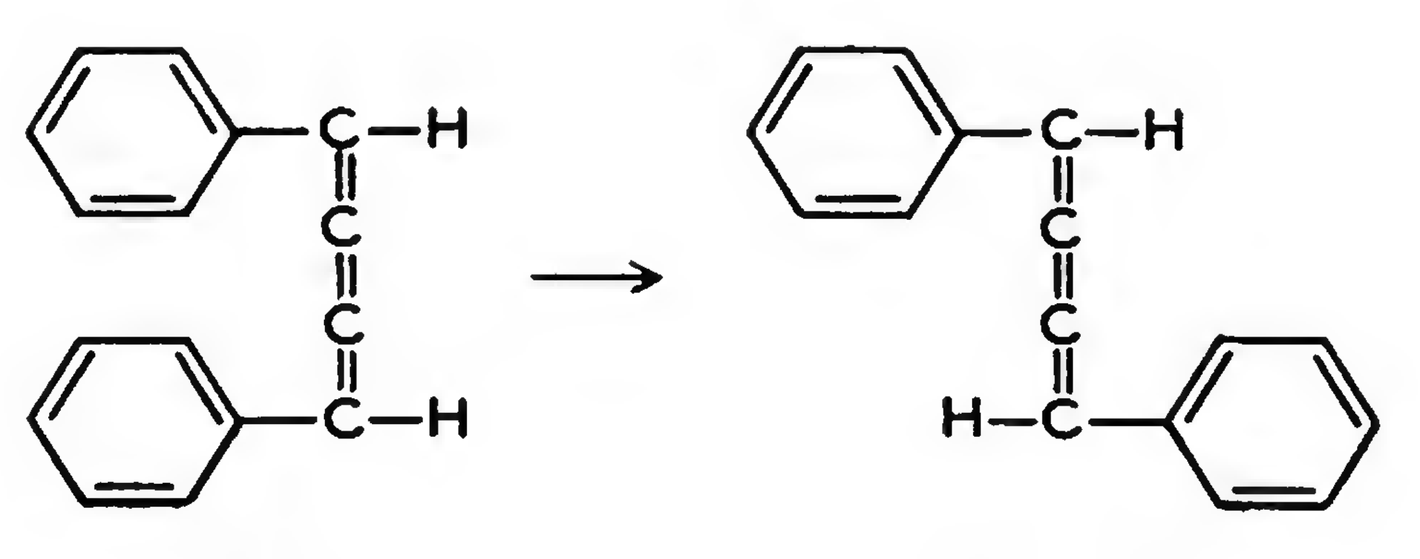
2. The use of acidic catalysts in the isomerization of allenic alkadienyl benzenes resulted in the formation of indenes. Alcoholic potash as catalyst led to the formation of an alkyne, whereas boiling decalin was effective in causing a racemization.

3. Non-allenic, aromatic alkadienes were observed to change into stable *trans* forms, a probable alkynyl benzene, an indane, and indenes.

ALKAPOLYENYL BENZENES

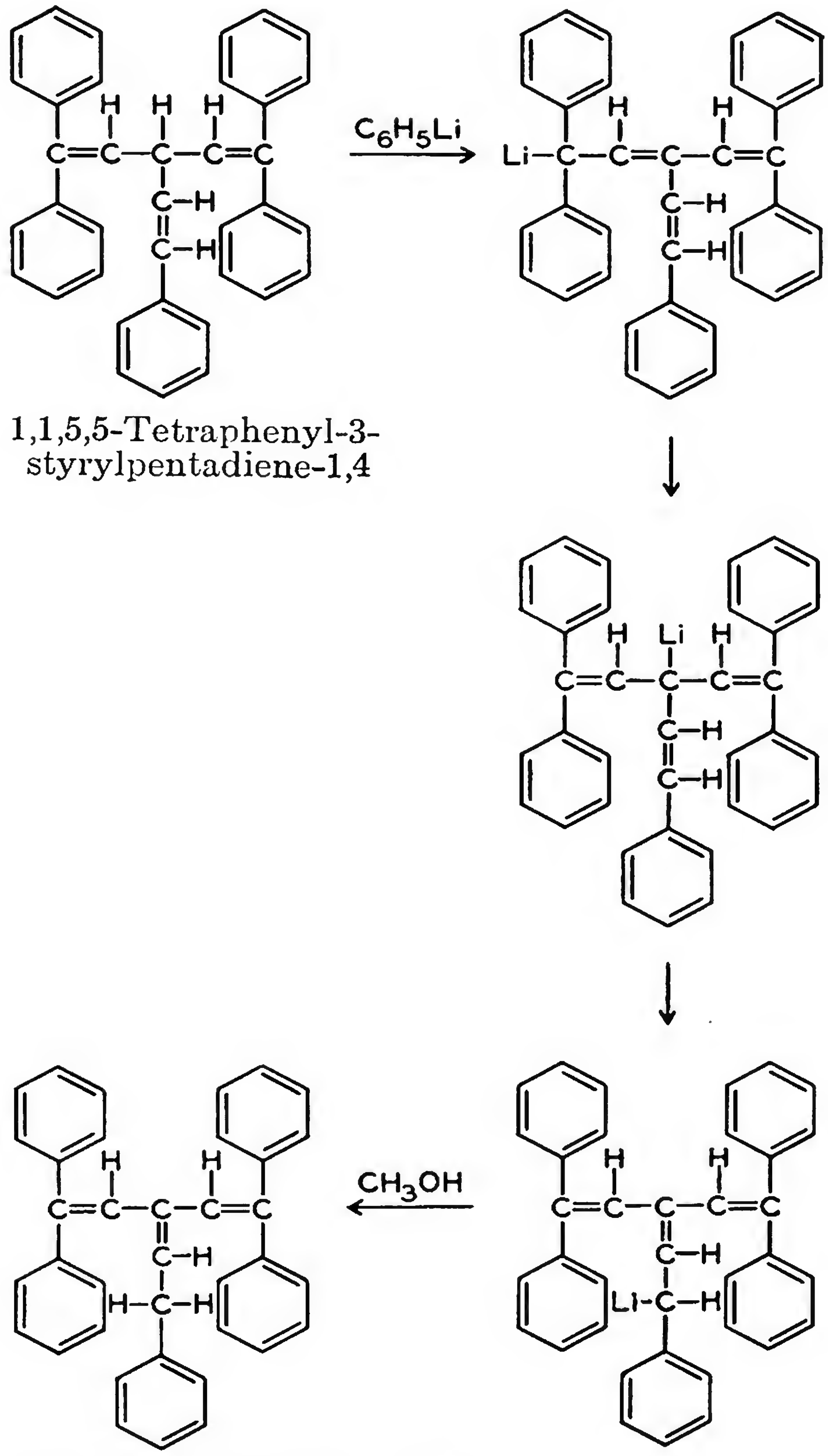
Isomerizations

1,4-Diphenylbutatriene is known in two geometrically isomeric forms: the stable *trans* form (m.p. 97°), and the liquid or unstable *cis* form. Both forms were originally taken for the *cis* and *trans* forms of 1,4-diphenylbutenyne,[572] but this is untenable when viewed from the standpoint that an exclusive formation of benzaldehyde occurs on oxidation.[229] On prolonged exposure to sunlight, the *cis* form isomerized to the stable *trans* form,[229, 572] especially when traces of iodine were present:[572]



[Cis] [Trans]

1,1,5,5-Tetraphenyl-3-styrylpentadiene-1,4 [*i.e.*, styrylbis (β,β-diphenylvinyl) methane], when treated with phenyl-lithium, gave a precipitate of a lithium derivative. The latter was then alcoholized, by an excess of methanol, into an isomer of the initial hydrocarbon: 1,1,5,5-tetraphenyl-3-phenethylidene-pentadiene-1,4 (*i.e.*, phenyl-[β,β-bis(β,β-diphenylvinyl) vinyl]methane or 1-benzyl-2,2-bis[β,β-diphenylvinyl]-ethylene of m.p. 130-131°).[654] The following triple "allyl tautomerism" was given as an explanation of the foregoing isomerization:[654]

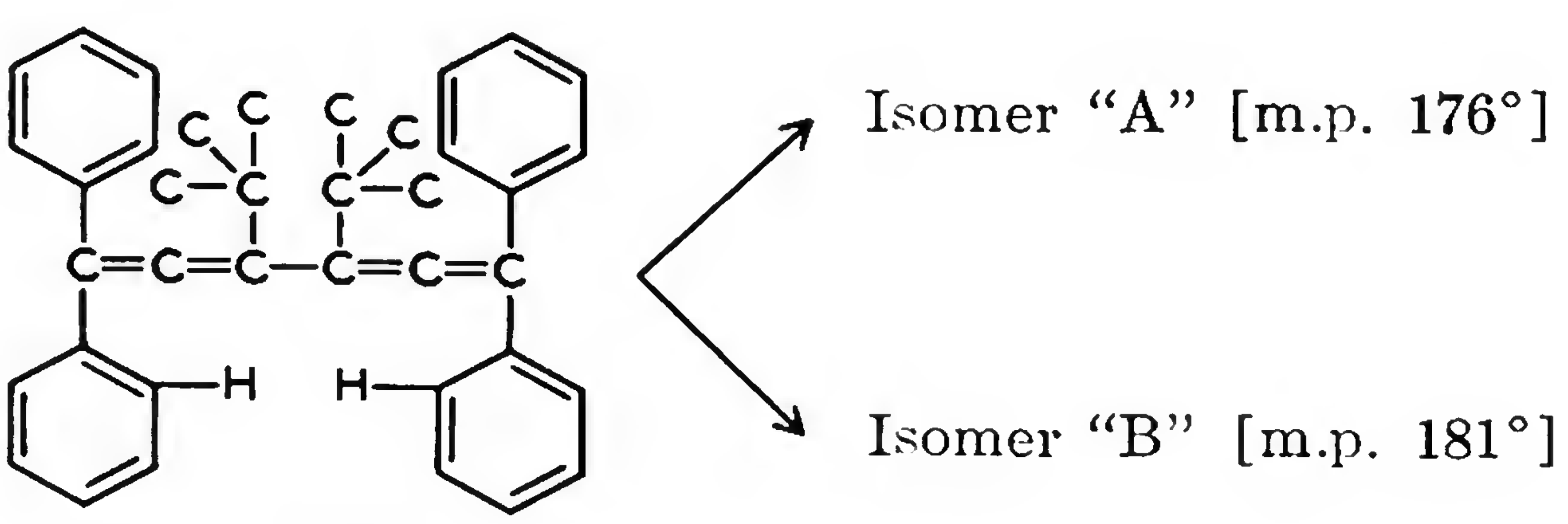


1,1,5,5-Tetraphenyl-3-styrylpentadiene-1,4

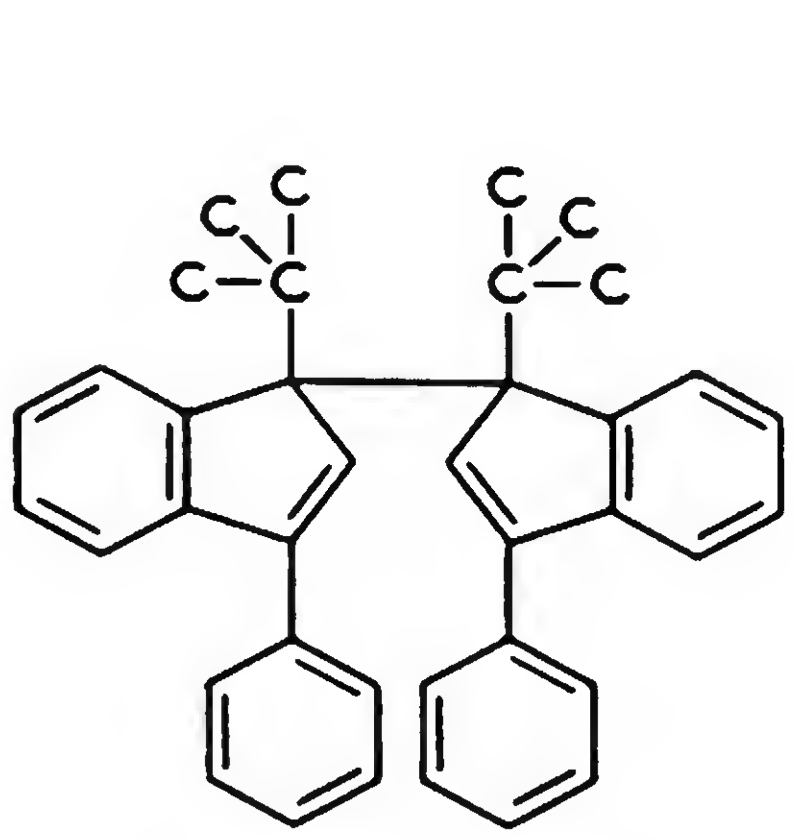
1,1,5,5-Tetraphenyl-3-phenethylidene-pentadiene-1,4

If one assumes the formation of the symmetrical lithium derivative as the logical first step of the isomerization, then the process is shortened into a simple "allyl transformation."

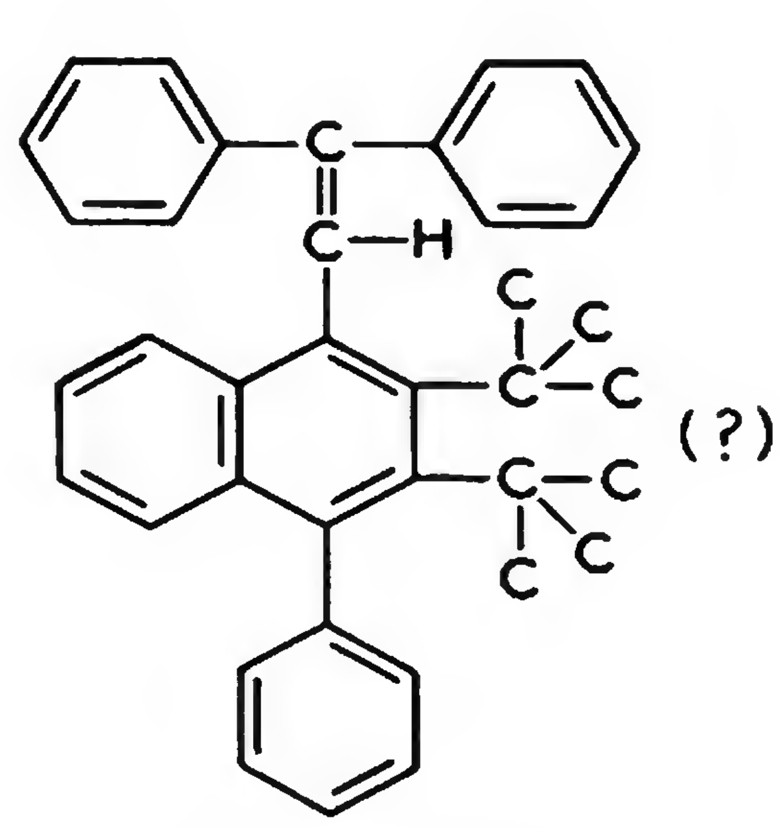
1,1,6,6-Tetraphenyl-3,4-di-*tert*-butyl-hexatetraene-1,2,4,5 (a diallenyl of m.p. 152°), upon treatment with acetic acid plus hydrogen chloride, was isomerized by a double cyclization to 1,1′-di-*tert*-butyl-3,3′-diphenyl-1,1′-biindene (the diindenyl "A" of m.p. 176°).[3, 175] However, the reports of one group of investigators,[3] in which the diallenyl (m.p. 152°) has been mistaken for the diindenyl, have caused considerable confusion. Later workers [175] proposed the diindenyl structure for the isomer of m.p. 176°. Recently,[360] it was stated that this isomer "A" cannot be the diindenyl. The arguments [217, 240, 360] are unconvincing, since they apply rather to the related 1,1′,3,3′-tetraphenyl-1-1′-biindene that theoretically should occur in meso and racemic forms (the existence of these forms was not proved). Treatment of the diallenyl (m.p. 152°) with sodium amalgam in the presence of ether gives still another isomer "B" (m.p. 181°) of unknown structure.[3, 175, 360] It has been suggested that the isomer "B" may be a substituted naphthalene.[360] The ultraviolet absorption spectra of isomers "A" and "B" showed no similarity with that of 2,8-diphenyl-6b,12b-dihydrochrysene and 2,8-diphenylchrysene. This fact was taken as evidence that "A" and "B" are not substituted 6b,12b-dihydrochrysenes.[360]



[m.p. 152°]



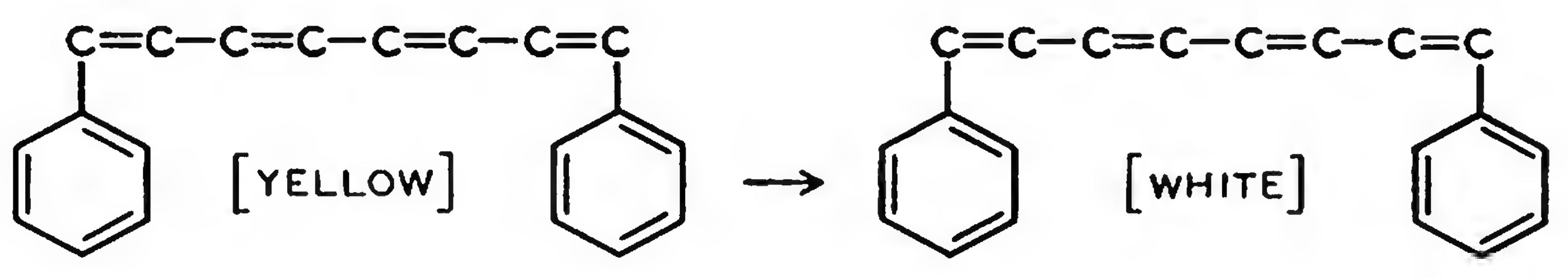
Isomer "A" [175]



Isomer "B"

1,8-Diphenyloctatetrene-1,3,5,7 exists in two stereo-isomeric forms: colorless (m.p. 124°) [184] and yellow (m.p. 225°).[190] The yellow form, when dissolved in chloroform containing free iodine and exposed to sun-

light for several days (in an atmosphere of carbon dioxide), gave the white form and a resin.[566] Similar results were obtained when the yellow solid was exposed to sunlight for 3 months in the presence of carbon dioxide. The reaction is apparently not reversible:



Isomerizations of alkapolyenyl benzenes are presented in Table 38, p. 380.

Conclusions.

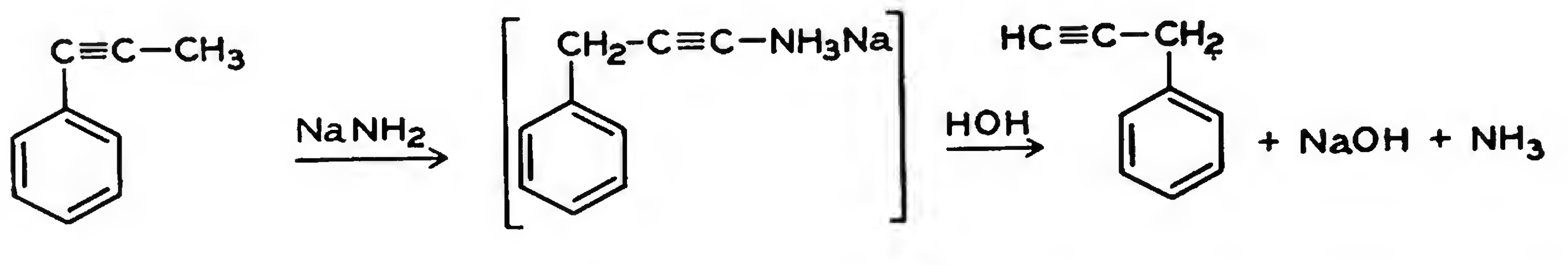
1. The alkapolyenyl benzenes exhibit several types of isomerization. The simpler changes comprise the conversion of a *cis* into the corresponding *trans* form, and the formation of a phenethylidene group from its styryl analog.

2. Cyclization in several directions is a factor that makes the study of one diallenyl difficult.

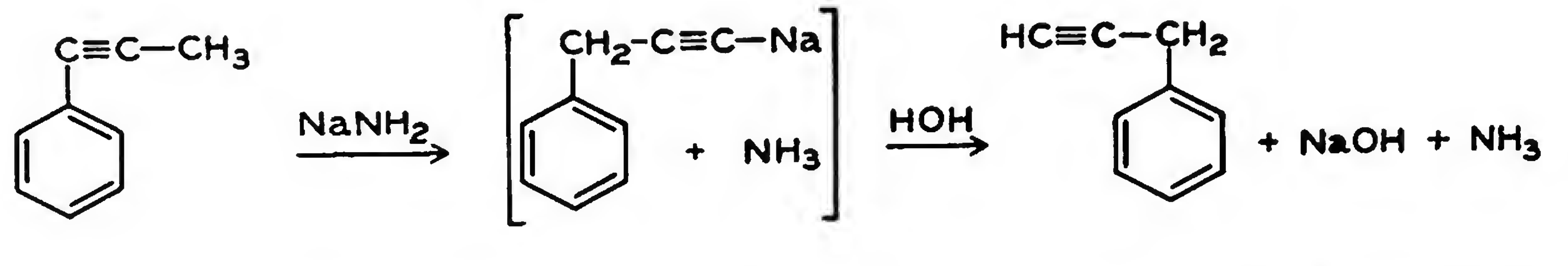
Alkynyl Benzenes

Isomerizations

1-Phenylpropyne-1 under the action of sodamide at 110° for 2 hours (with toluene as diluent), followed by hydrolysis of the intermediary organosodium derivative, was isomerized into 3-phenylpropyne-1.[80, 81] This reaction apparently proceeds as follows: [82]

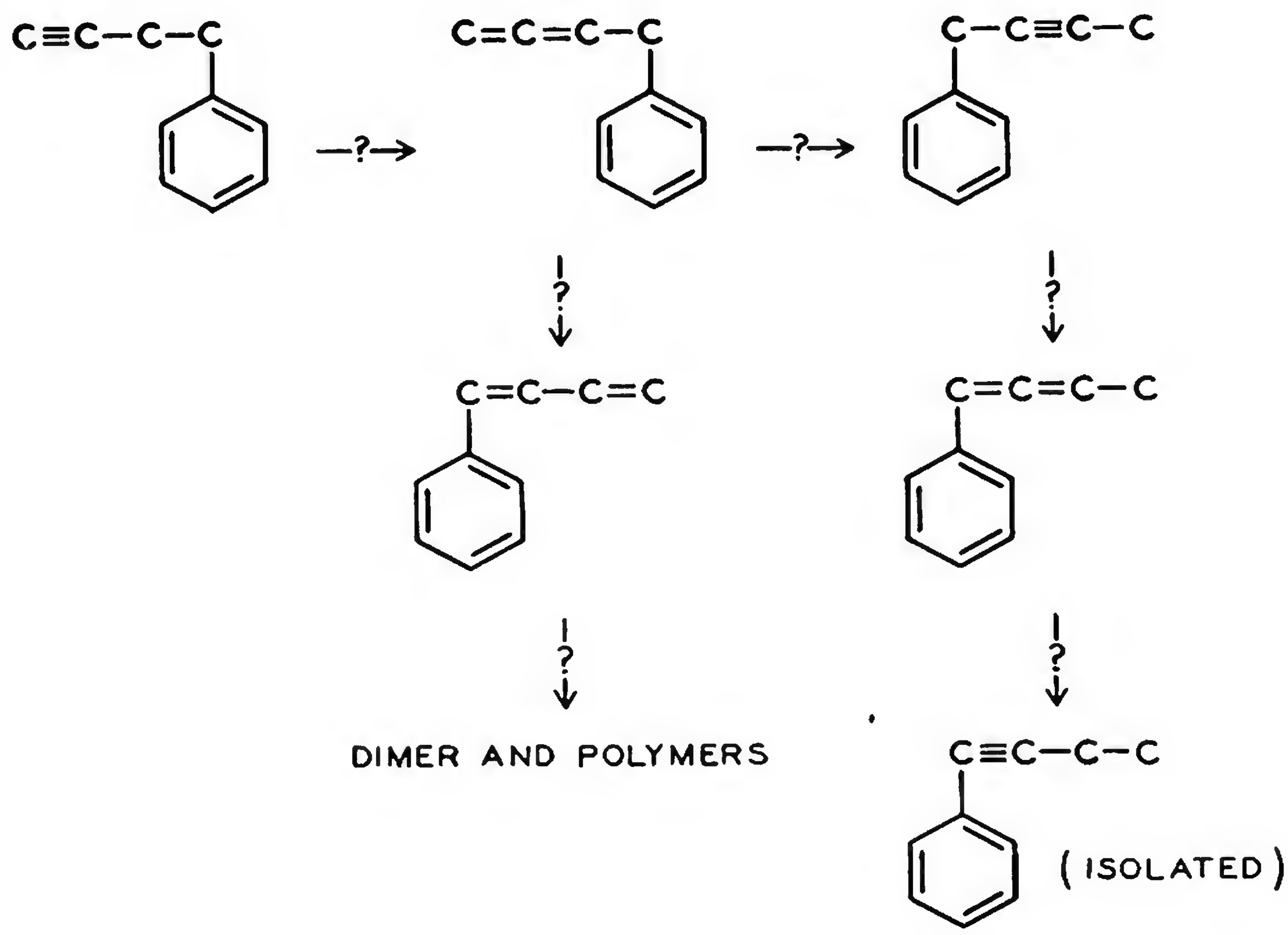


Intermediary formation of sodium benzylacetylide plus ammonia serves as alternative explanation of this isomerization:



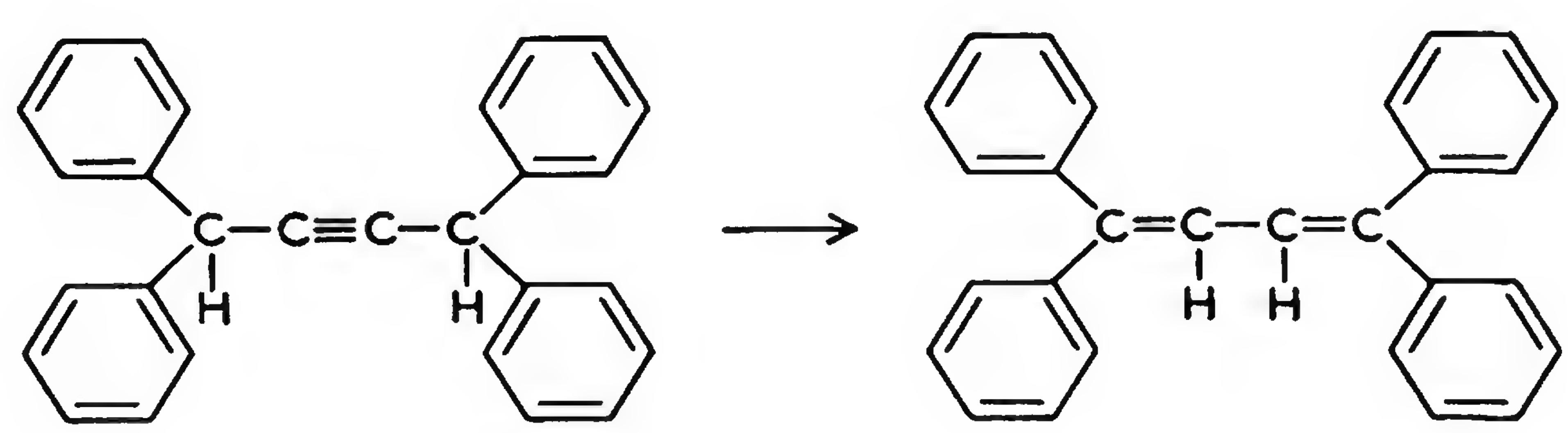
4-Phenylbutyne-1 formed less than 25 per cent of 1-phenylbutyne-1 and 75 per cent of polymers upon passage over chromia at 250° in a stream of carbon dioxide.[344a] The course of the isomerization was con-

sidered to be successive formations of 4-phenylbutadiene-1,2, 1-phenylbutyne-2, 1-phenylbutadiene-1,2, and 1-phenylbutyne-1; conversion of 4-phenylbutadiene-1,2 into 1-phenylbutadiene-1,3 would account for the extensive polymerization:

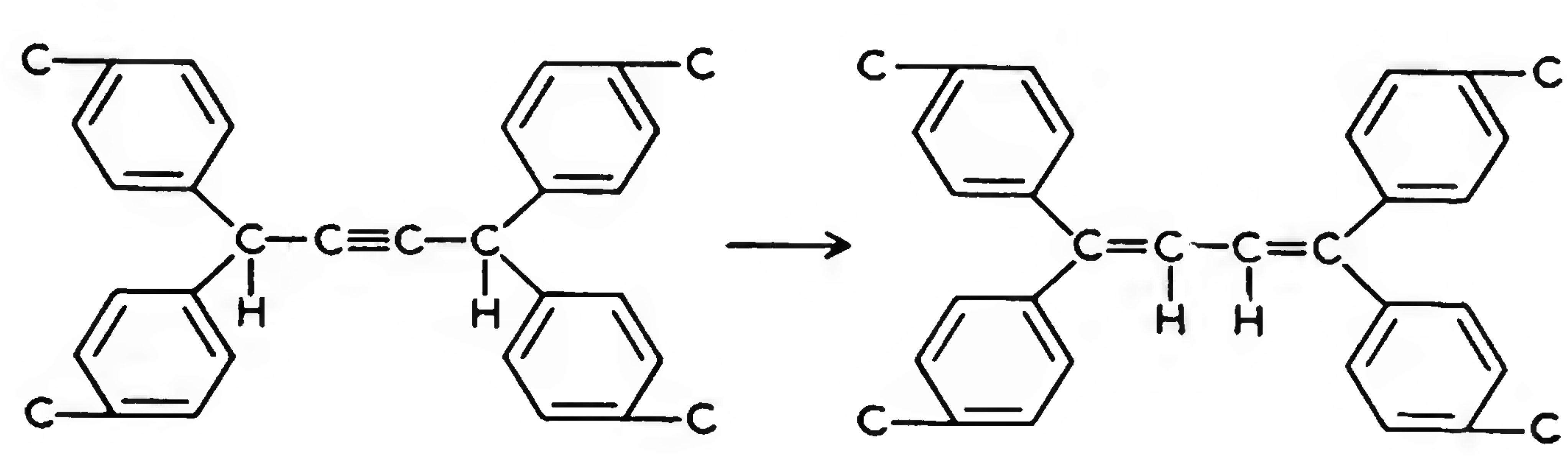


4-Phenylbutyne-1 when passed over "Floridin" at 250° probably yielded a small amount of 4-phenylbutadiene-1,2, *i.e.*, benzylallene.[555]

1,1,4,4-Tetraphenylbutyne-2, heated with alcoholic sodium ethoxide, was converted into 1,1,4,4-tetraphenylbutadiene-1,3: [84, 85]

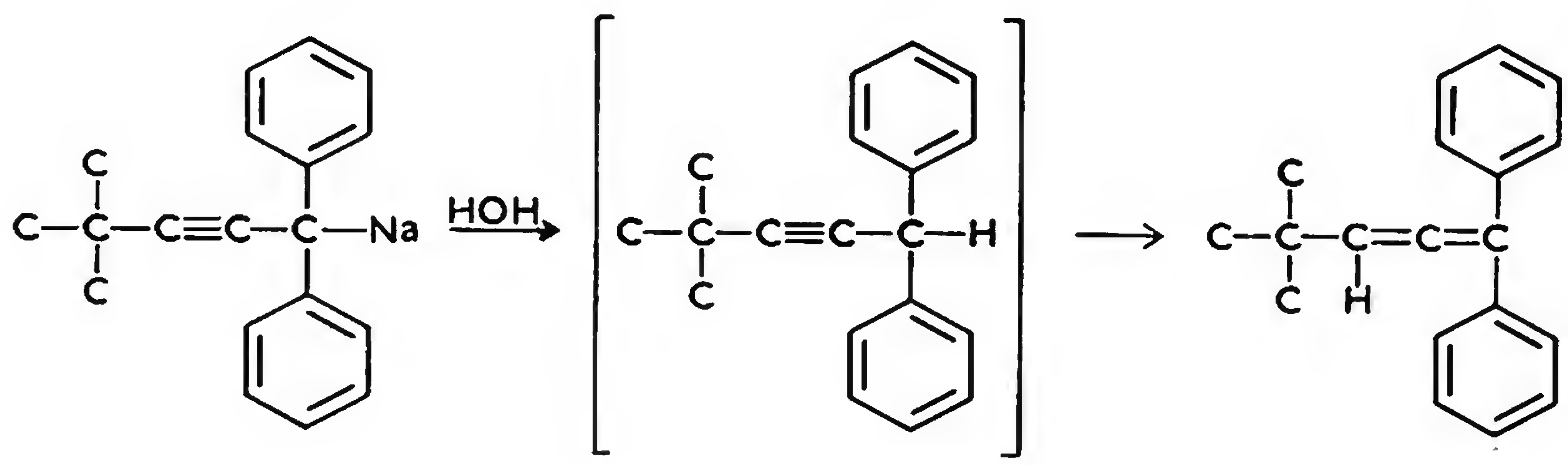


1,1,4,4-Tetra-*p*-tolybutyne-2, heated under reflux for 3 hours with alcoholic sodium ethoxide, was isomerized to 1,1,4,4-tetra-*p*-tolybutadiene-1,3: [86]



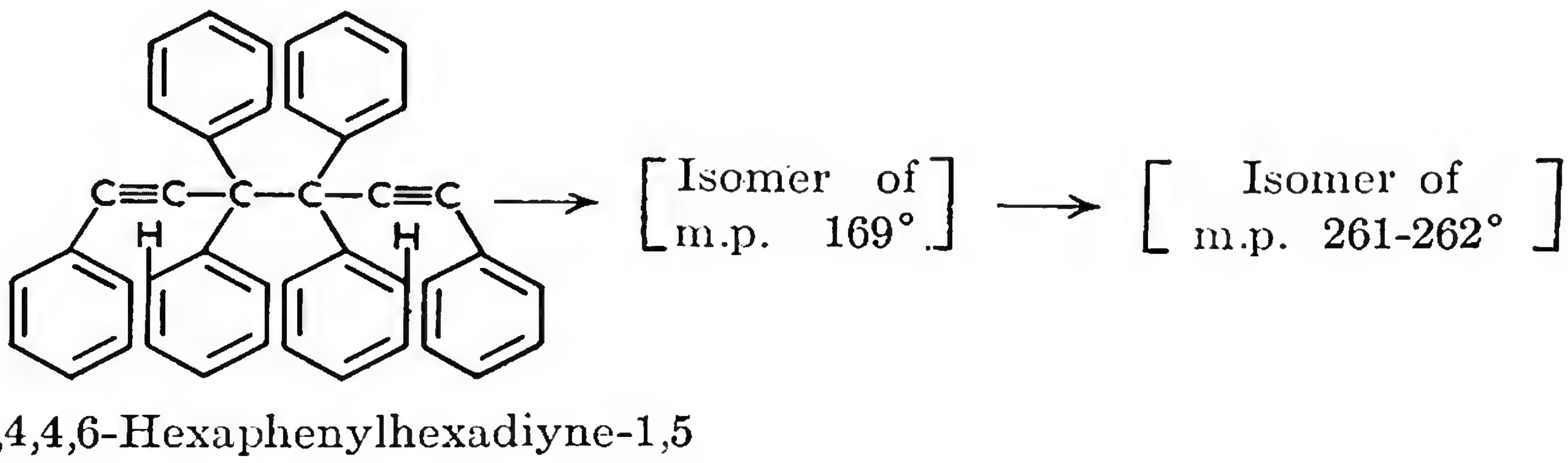
Treatment of 2,2,9,9-tetramethyl-5,5,6,6 - tetraphenyldecadiyne - 3,7 (*i.e.*, 1,2-di-*tert*-butylethynyl-tetraphenylethane) with 40 per cent

sodium-amalgam yielded diphenyl-*tert*-butylethynylmethylsodium (*i.e.*, a pentyne derivative). Hydrolysis[564] of this organosodium compound gave an allene, probably via the corresponding alkyne. This reaction is of interest in connection with the theory of isomerization of aliphatic allenes and alkynes. The present non-formation of an alkyne-1 (with sodium amalgam as "catalyst") is due to an interference in hydrogen migration (a blocking caused by presence of specific methyl and phenyl groups):



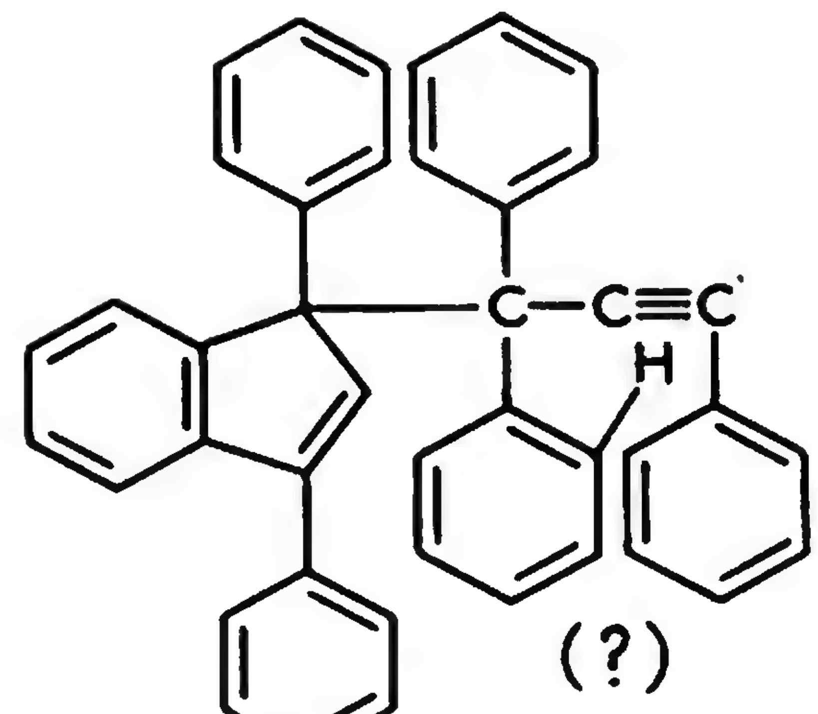
(Compare this scheme with the shift of a methyl group within 4,4-dimethylpentadiene-1,2).

1,3,3,4,4,6-Hexaphenylhexadiyne-1,5 (in petroleum ether) was converted in one hour at room temperature into an isomer of unknown structure (m.p. 169° when "pure").[393] The new isomer was found to be identical with a hydrocarbon (m.p. 179°) obtained by the coupling of phenethynyl(diphenyl)methyl.[389] The hydrocarbon of m.p. 179°, however, was erroneously considered to be 1,3,3,4,4,6-hexaphenylhexadiyne-1,5. A sample of the foregoing coupled-hydrocarbon (m.p. 172-173°), when boiled with acetic acid saturated with hydrogen chloride, gave still another isomer of unknown structure (m.p. 261-262°).[240] Knowledge of the course of these isomerizations is limited; they apparently involve two successive cyclizations:

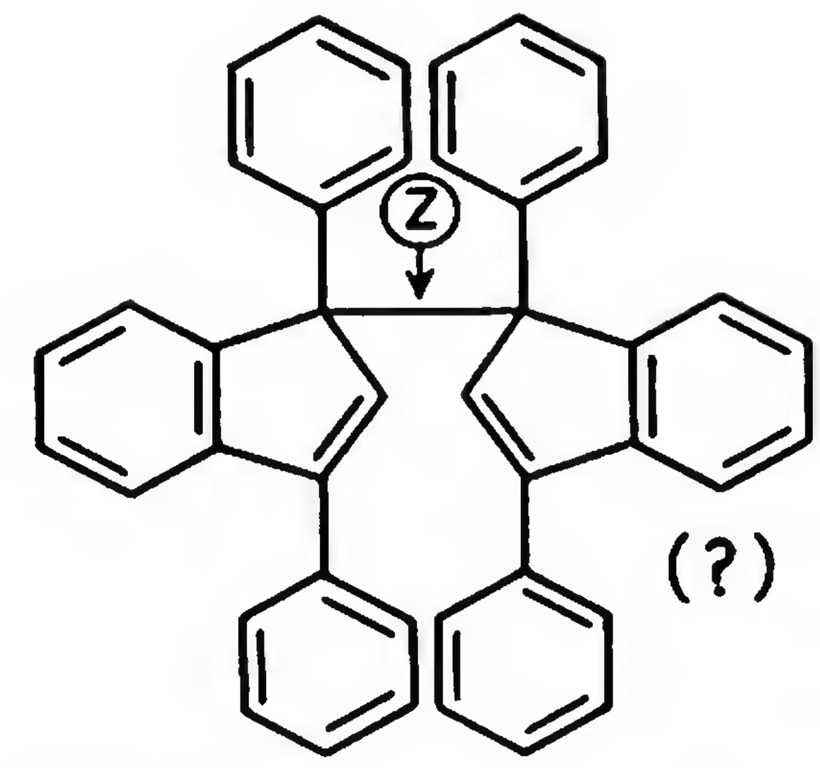


1,3,3,4,4,6-Hexaphenylhexadiyne-1,5

The isomer of m.p. 169° [179°, 172-173°] may have the structure of 1-(1,1,3-triphenylpropargyl)-1,3-diphenylindene, whereas the isomer with m.p. 261-262° is probably 1,1′,3,3′-tetraphenyl-1,1′-biindene [*i.e.*, bis-1,1′-(1,3-diphenylindenyl)]:


(?)

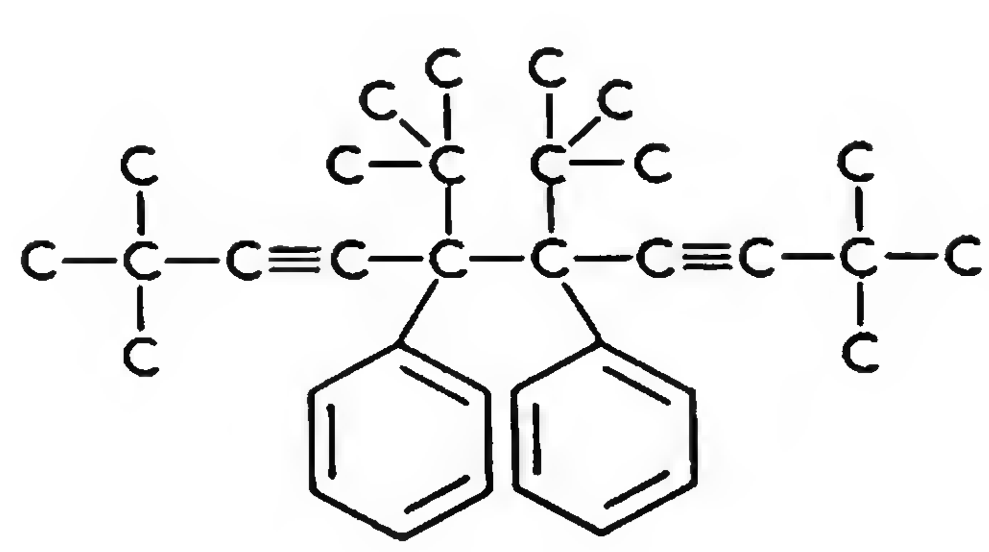
[Isomer of m.p. 169°]


(?)

[Isomer of m.p. 261-262°]

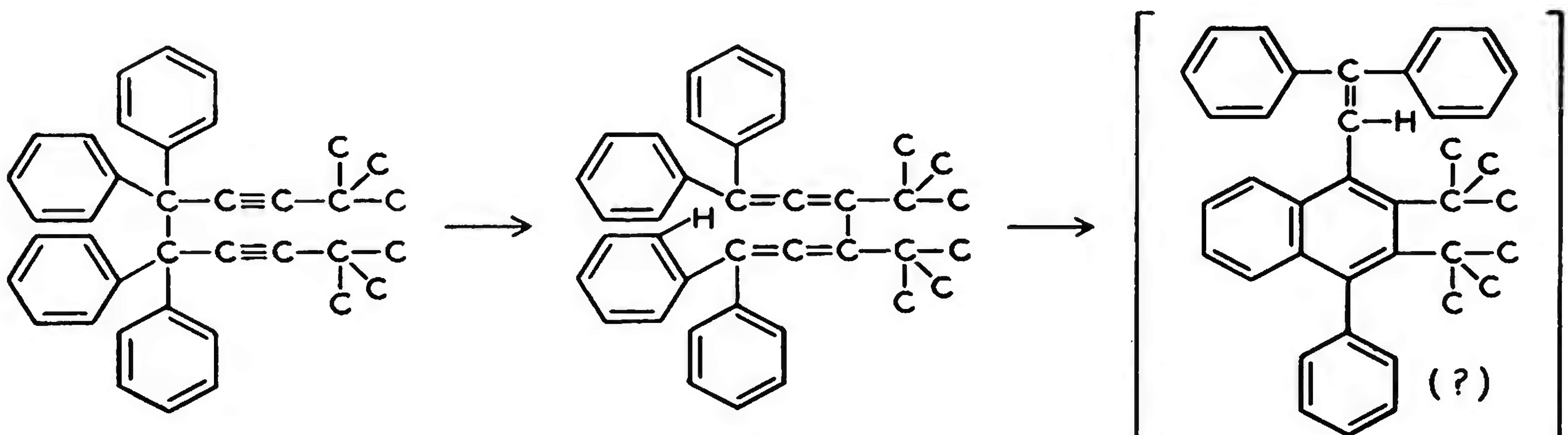
The opinion has been expressed[240] that the isomers (m.p. 169° and 261-262°) cannot be the substituted-diindenyl (*i.e.*, 1,1′,3,3′-tetraphenyl-1,1′-biindene). The arguments[217, 240] supporting this opinion are unconvincing, since the substituted diindenyl (synthesized) dissociates readily. Moreover, the position of the diyl bridge "Z" (*infra*) in the supposed true synthetic (m.p. 190-191°) remains unproved to date. Another investigator[648] considers the corresponding monoindenyl structure to be more plausible for the m.p. 261-262° isomer than the diindenyl formula, disregarding the fact that the "indene" is a precursor of the "diindenyl." The recent synthesis of a substituted 6b,12b-dihydrochrysene[360] suggests an investigation of the isomerization products for the presence of 2,6b,-8,12b-tetraphenyl-6b,12b,-dihydrochrysene. On the other hand, one should not overlook the possible presence of tetraphenyldihydronaphthacene-related hydrocarbons, which have been emphasized in the coupling of substituted triethynylmethyl halides.[562] The isomer of m.p. 179°, when heated in xylene solution with various oxidizing substances,[648] or merely fused,[389, 647] gave a yellow isomer with m.p. 225°[648] or 249°.[647]

A possible although unreported isomerization of 2,2,9,9-tetramethyl-5,6-di-*tert*-butyl-5,6-diphenyldecadiyne-3,7 (*i.e.*, 1,2-di-*tert*-butyl-1,2-di-*tert*-butylethynyl-diphenylethane) into a stable isomer may occur in the reaction between (*tert*-butyl) (*tert*-butylethynyl) (phenyl) methyl bromide and sodium amalgam (in the presence of ether).[192]


[Isomerizes?]

2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7 (*i.e.*, 1,2 - di-*tert*-butylethynyl-tetraphenylethane), upon standing at room temperature in ether, was isomerized to the diallenyl, 1,1,6,6-tetraphenyl-3,4-di-*tert*-butyl-hexatetrene-1,2,4,5 (m.p. 153°). This reaction was completed

within 12 hours, but when the ethereal solution was heated to 50°, the isomer was formed in a few minutes.[564] Acetone, hexane, and heptane can be used also as solvents. The structure of the isomer is given in a recent publication.[175] Treatment [564] of 1,2-di-*tert*-butylethynyl-tetraphenylethane with ether plus one per cent sodium-amalgam for several days, followed by alcohol, gave an "impure isomer" that probably was a mixture [3] of the diallenyl (m.p. 153°) and its isomer "B" (m.p. 181°) encountered in the previous section on "Alkapolyenyl Benzenes":

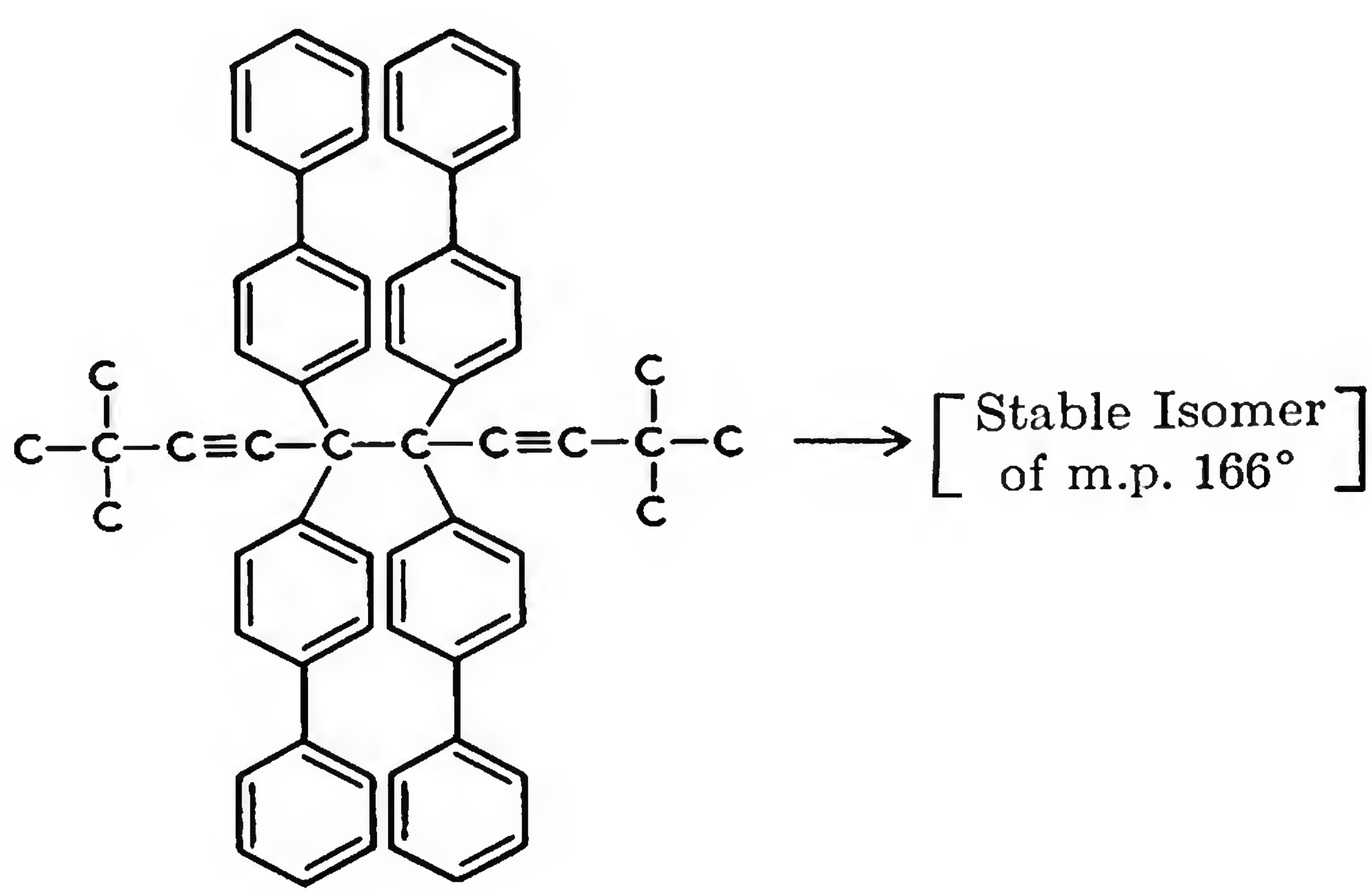


2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyl-decadiyne-3,7

1,1,6,6-Tetraphenyl-3,4-di-*tert*-butyl-hexatetrene-1,2,4,5

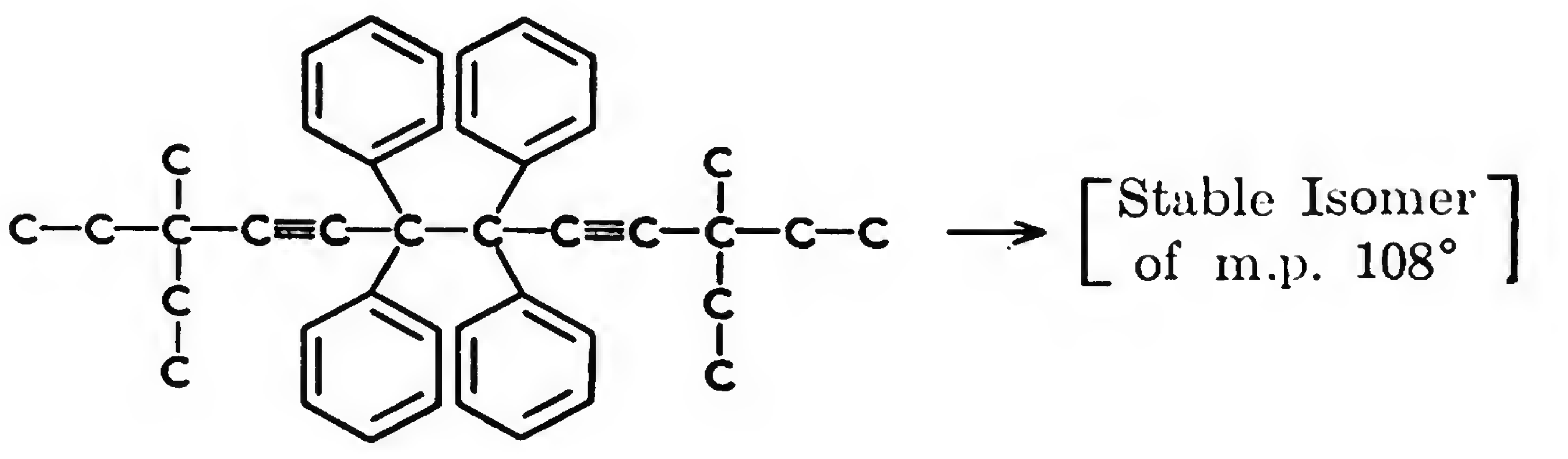
1-(β,β-Diphenyl-vinyl)-2,3-di-*tert*-butyl-4-phenyl-naphthalene (?) [Isomer "B"]

2,2,9,9-Tetramethyl-5,5,6,6-tetra-biphenylyldecadiyne-3,7 (*i.e.*, 1,2-di-*tert*-butylethynyl-tetra-biphenylylethane) was converted into an isomer (m.p. 166°) upon standing in toluene at room temperature for 10 hours.[592] The structure of the isomer is unknown. Half of the molecule probably retains its original carbon skeleton, since a 50 per cent yield of di-biphenylyl ketone results upon oxidation of the new isomer by oxygen:



3,10-Dimethyl-3,10-diethyl-6,6,7,7-tetraphenyl-dodecadiyne-4,8 [*i.e.*, 1,2-di-(3-methyl-3-ethylpentynyl-1)-tetraphenylethane] isomerized at 0°

in a short time without a solvent, or at room temperature in the presence of ether.[242] The structure of the isomer is unknown, but there is some evidence that half of the molecule retains its original carbon skeleton: [242]



Isomerizations of alkynyl benzenes are presented in Table 39, p. 382.

Conclusions

1. Alkynyl benzenes isomerize by hydrogen transfers, the extent of which varies considerably depending on the initial isomer.

2. 1,2-Di-*tert*-butylethynyl-tetraphenylethane exhibits no evidence of labile hydrogen activity in the presence of ether. However, when treated with sodium amalgam plus water, it forms an allenic scission product containing a hydrogen atom derived from the water.

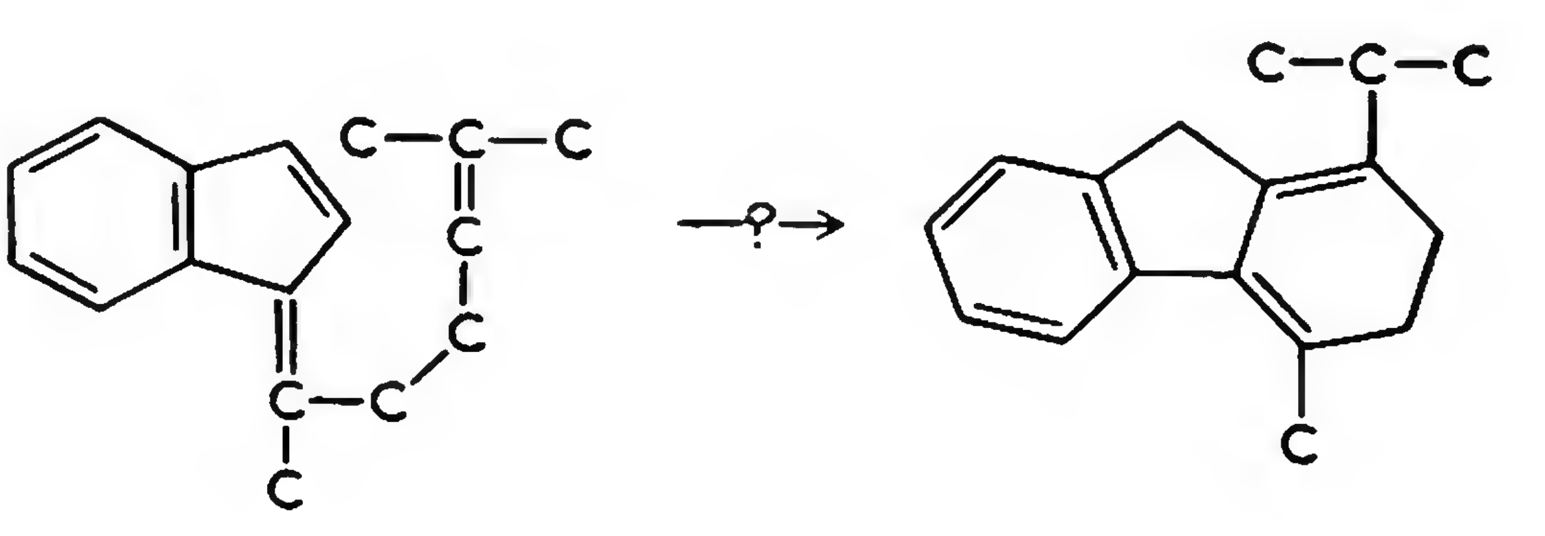
3. Isomerizations of aryl propyne and of aryl butynes involve the migration of two hydrogen atoms.

Condensed Aromatics

The condensed aromatic hydrocarbons comprise members of the indenes, fluorenes, naphthalenes, anthracenes, phenanthrenes, naphthacenes, and other fused-polycyclic systems. These members are discussed in the enumerated order. Isomerizations of more complex indenes are presented in the section on "Aromatic-Cyclene Hydrocarbons."

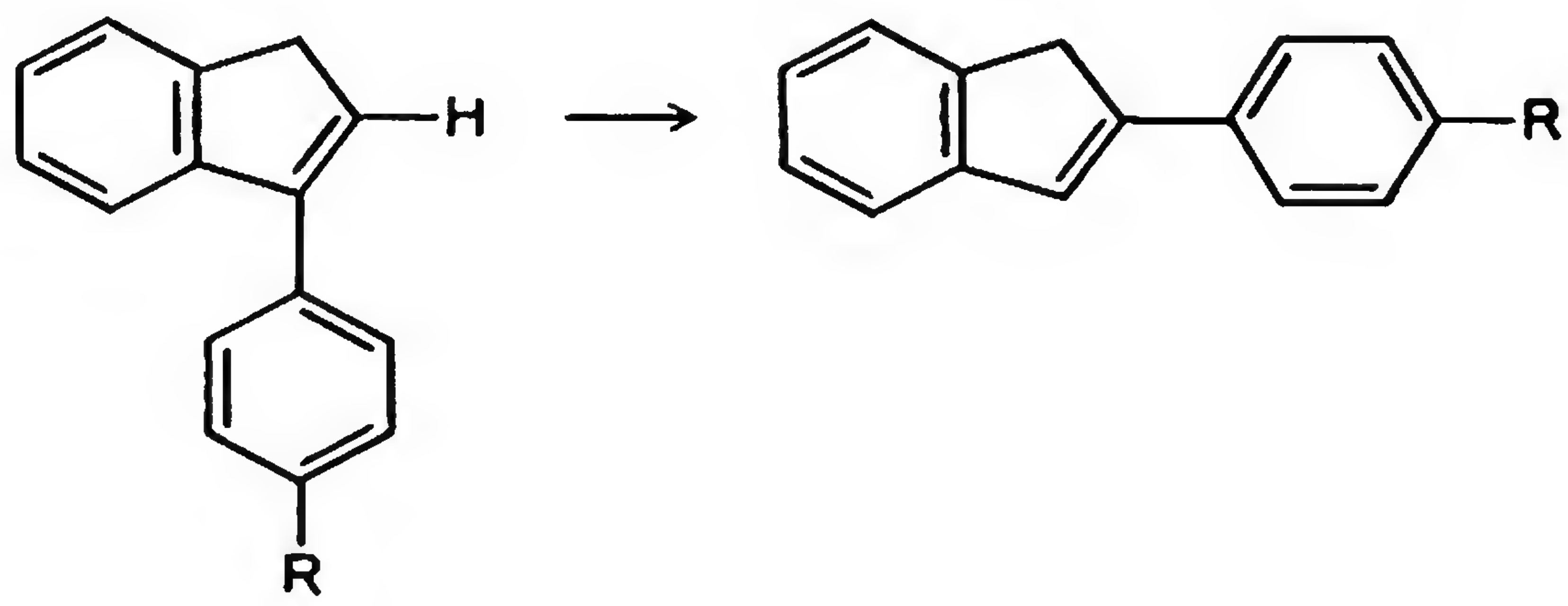
Indanes and Indenes

1-(1,5-Dimethyl-4-hexenylidene) - indene (*i.e.*, "methylisohexenylbenzofulvene"), when heated at 140° for 12 hours with formic acid, gave a tricyclic isomer, probably 1-isopropyl-4-methyl-2,3-dihydrofluorene: [491]

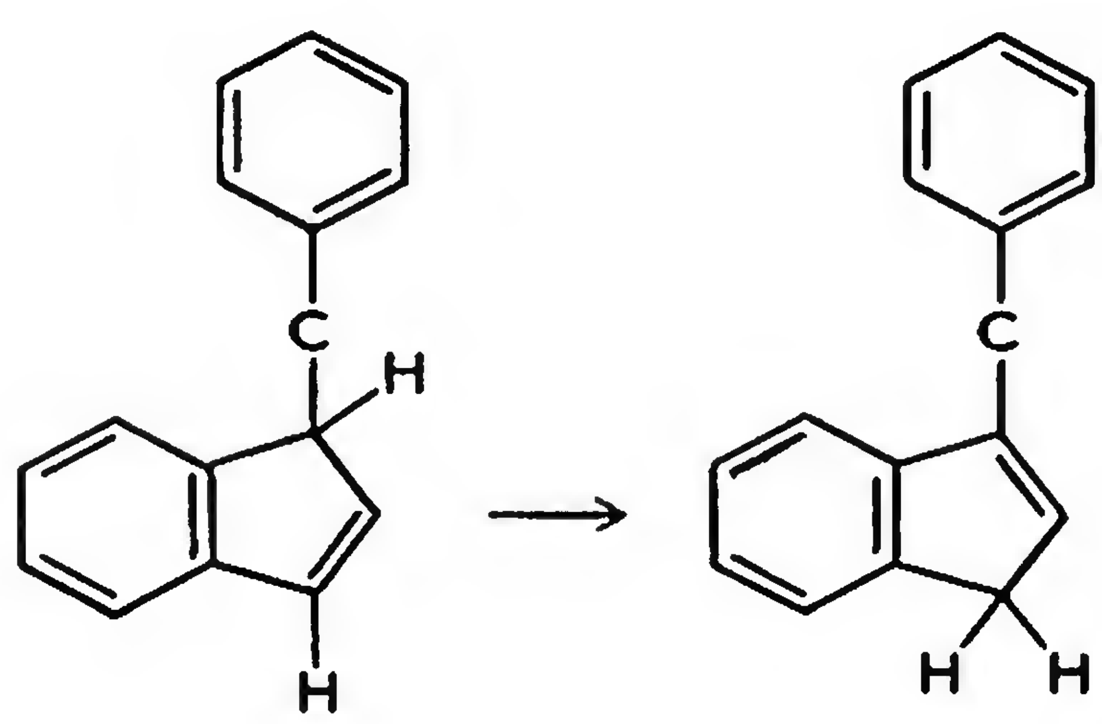


3-Phenylindene and 3-*p*-tolylindene, passed as vapors in a carbon dioxide atmosphere over pumice heated to a dark-red heat (16 mm. Hg

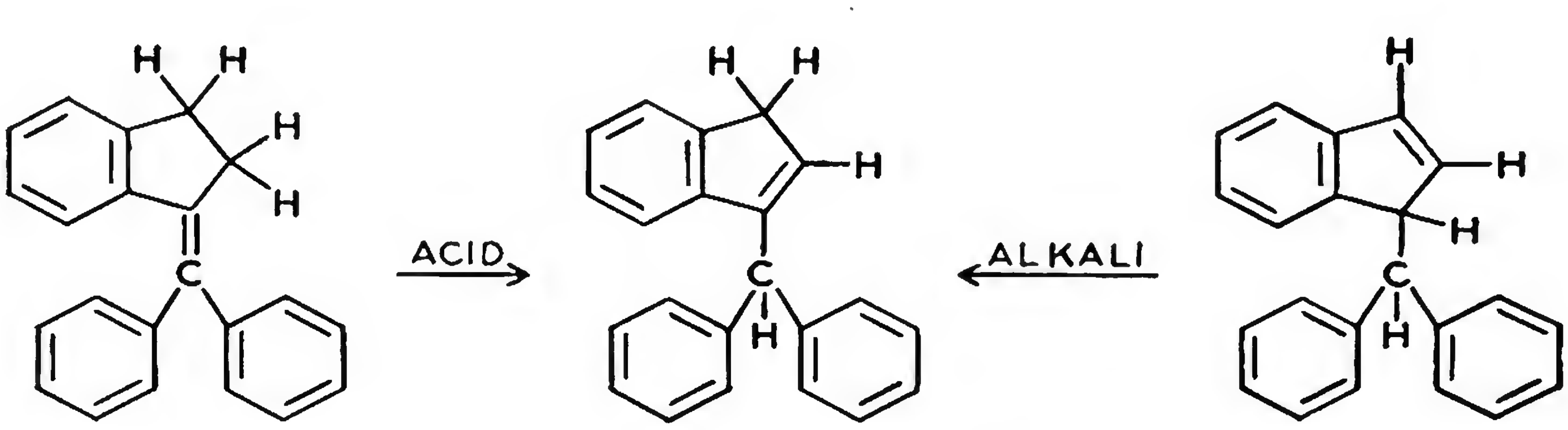
pressure), gave the 2-derivatives in yield of 33 and 16.5 per cent, respectively[88] ("R" is H or CH_3):



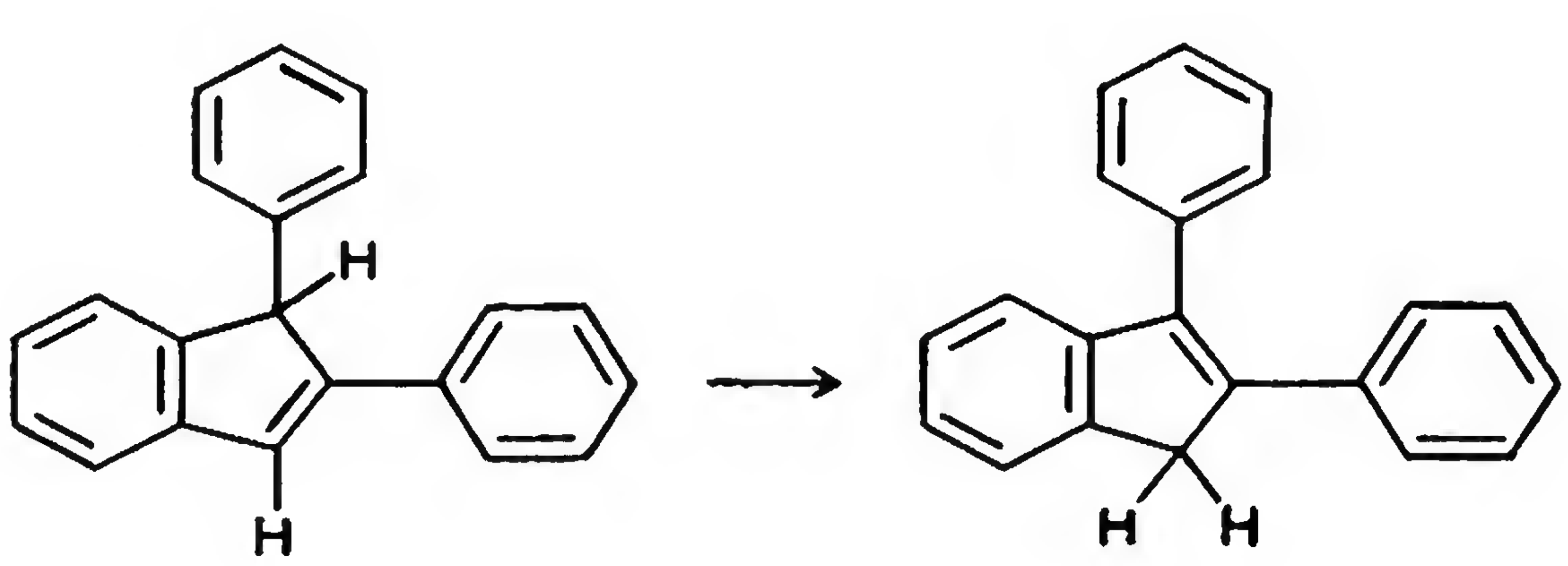
1-Benzylindene, upon treatment with potassium methoxide solution, gives 3-benzylindene.[126, 127] This isomerization involves obviously only an allylic-type of hydrogen migration, regardless of the confusion caused by a change in numbering from 1- to 3-benzyl:



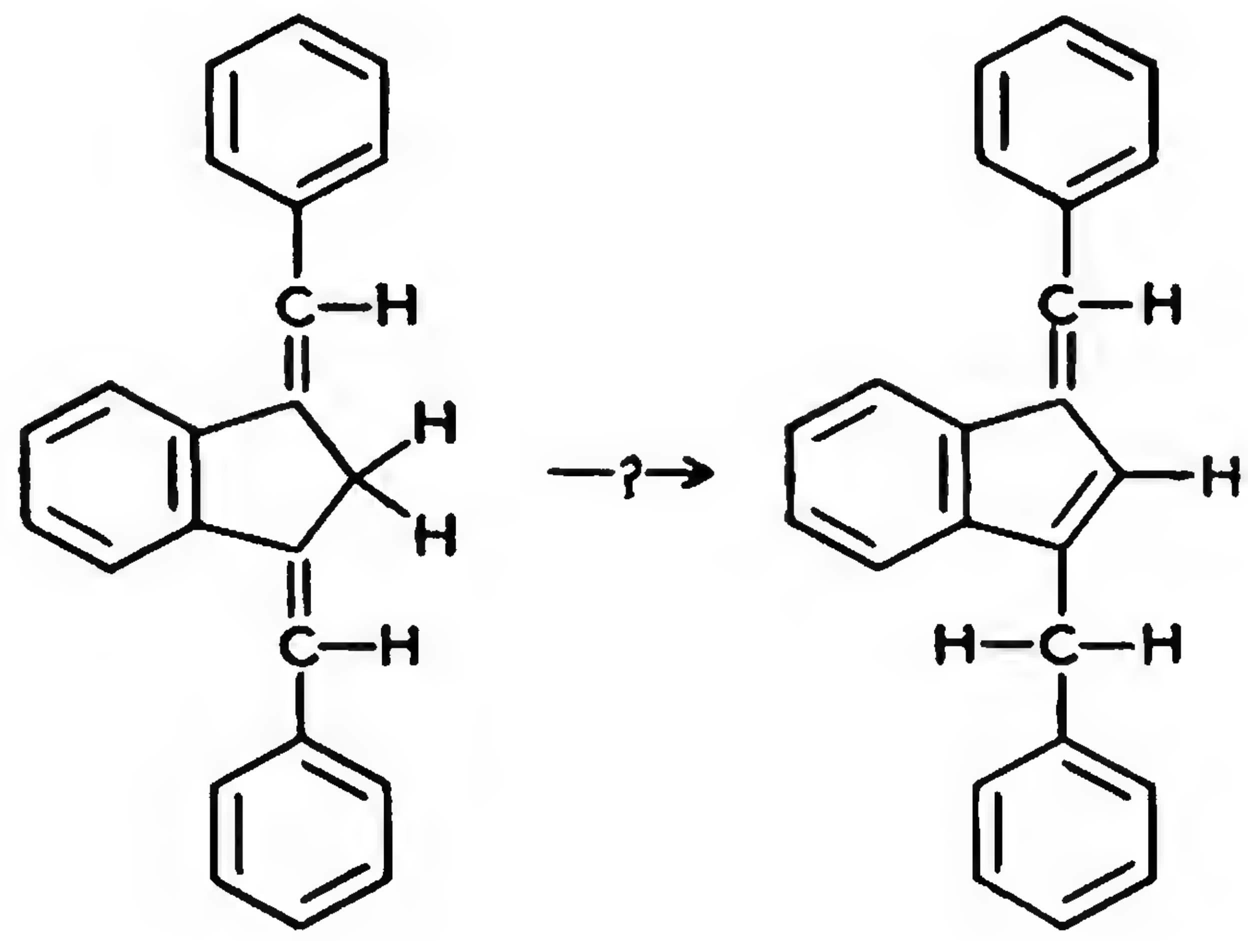
1-Diphenylmethylene-indane, heated with concentrated hydrochloric acid, forms 3-benzhydrylindene.[126] The shift of the double bond into the adjacent ring is patterned after the isomerization of terpinolene. 1-Benzhydrylindene, when treated with potassium methoxide solution, gives 3-benzhydrylindene also.[126, 127] The different roles of acid and alkali serve to clarify the course of these reactions:



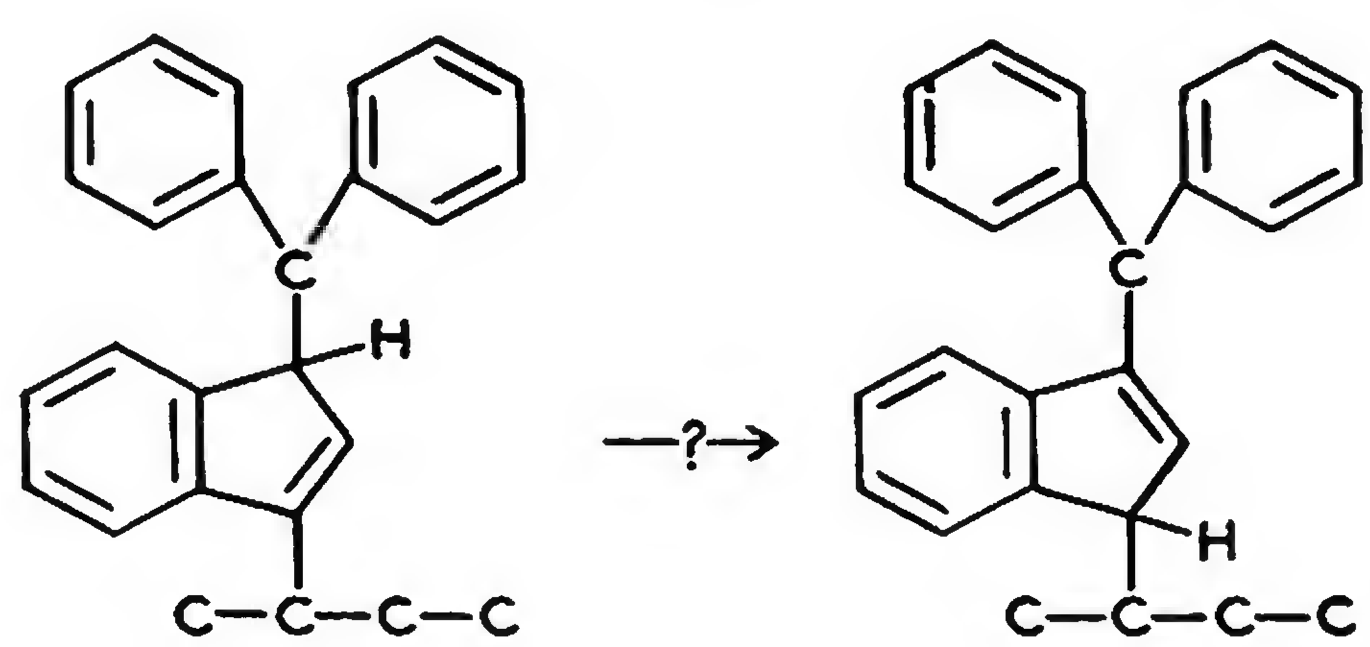
1,2-Diphenylindene, when boiled with alcoholic potash, yields a precipitate of 2,3-diphenylindene.[69, 428] This isomerization obviously involves only an "allylic" migration of hydrogen:



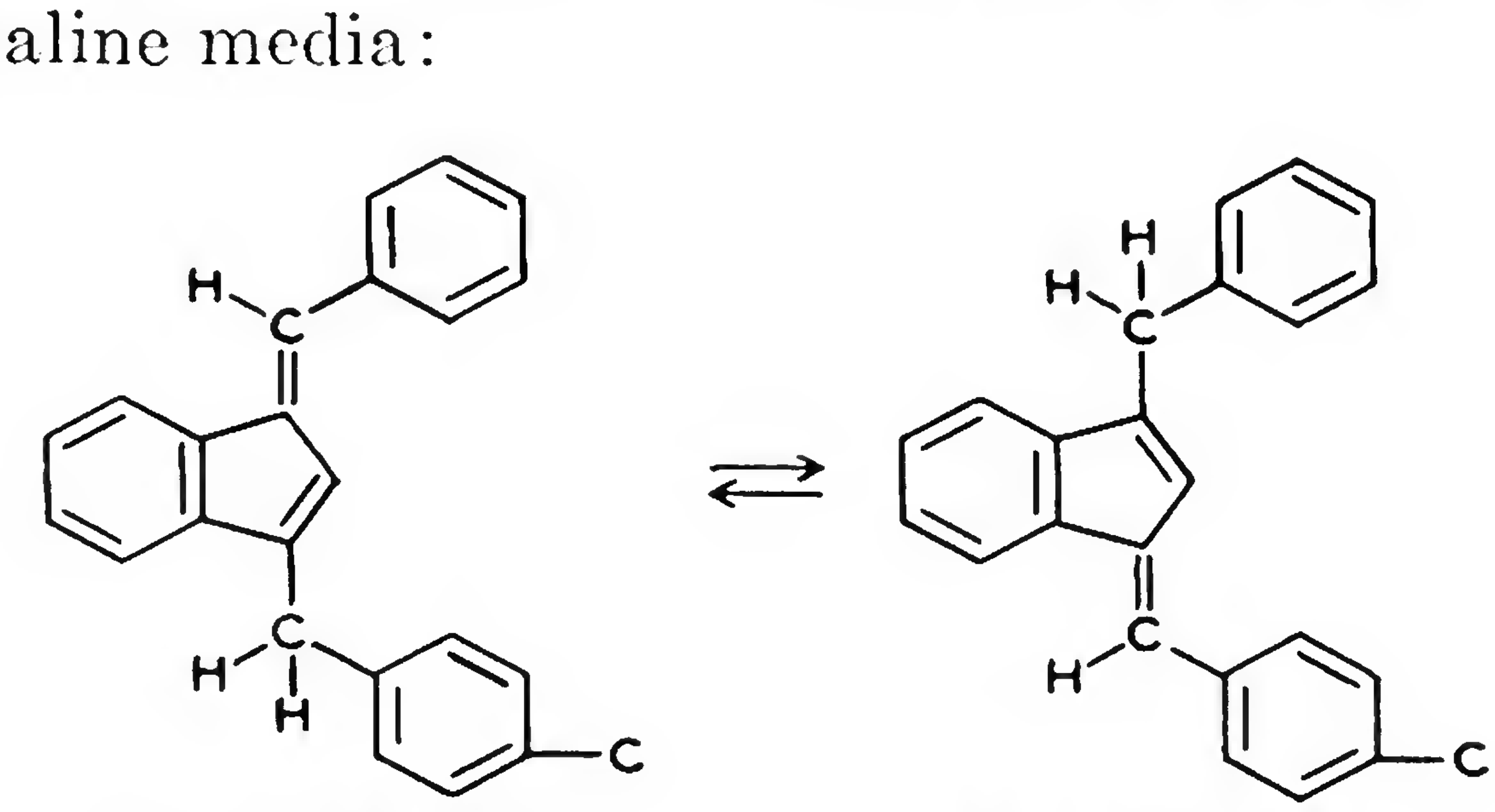
1,3-Dibenzylidene-indane is the structure proposed by the authors for a colorless compound, $C_{23}H_{18}$, of m.p. 213°. The latter underwent a slow change into the yellow 1-benzylidene-3-benzylindene when heated at a temperature over 213° or when subjected to vacuum distillation: [579]



1-Benzhydryl-3-*sec*-butyl-indene, likewise, is the structure proposed by the authors for a colorless compound (m.p. 121-123°) which, boiled with potassium methoxide solution, gives another colorless isomer (m.p. 94-95°).[656] The last isomer is probably 1-*sec*-butyl-3-benzhydrylindene:

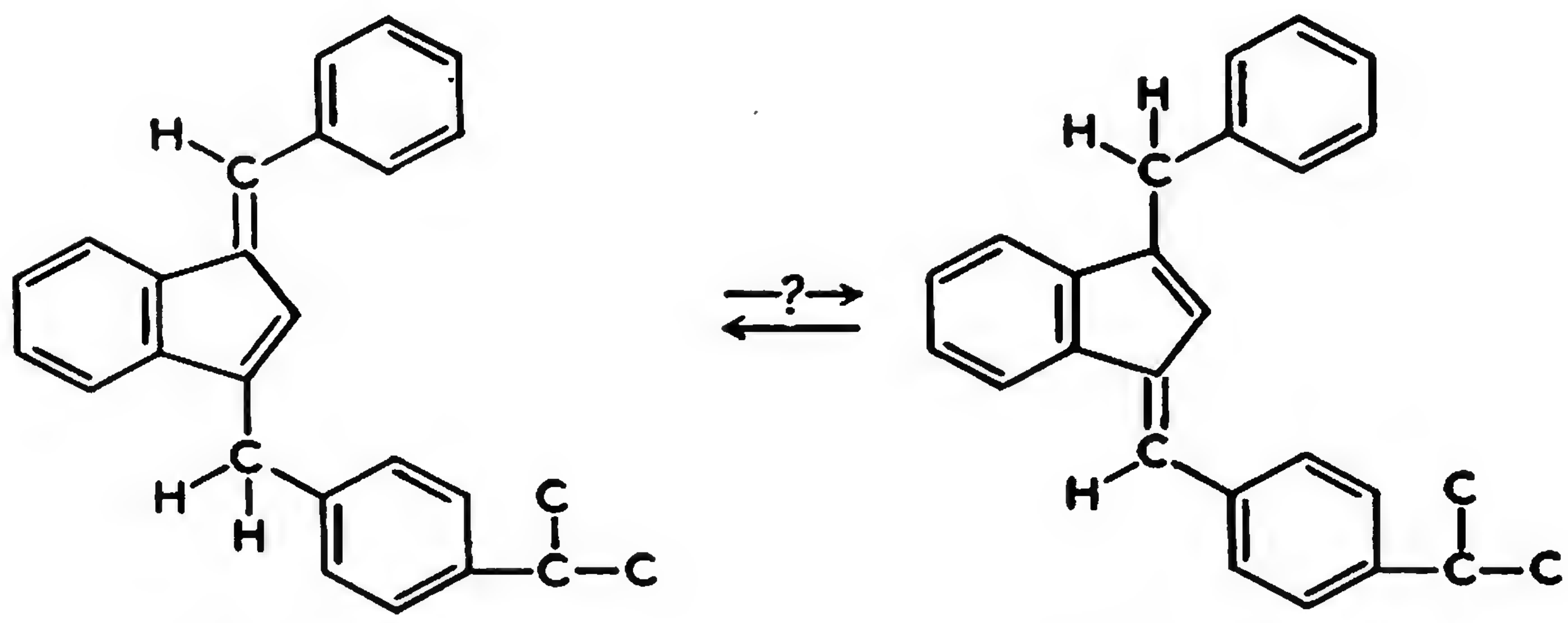


1-Benzylidene-3-*p*-methylbenzyl-indene and 1-*p*-methylbenzylidene-3-benzylindene both form the same equilibrium mixture (m.p. 70°) when boiled with methanolic potash.[59] 1-*p*-Isopropylbenzylidene-3-benzyl-indene, when boiled with potassium methoxide solution, also gives an "equilibrium mixture" (m.p. 71-73°) containing some newly formed 1-benzylidene-3-*p*-isopropylbenzylindene.[59] These isomerizations are merely an *endo-exo* oscillation of 2 conjugated double bonds under the influence of alkaline media:



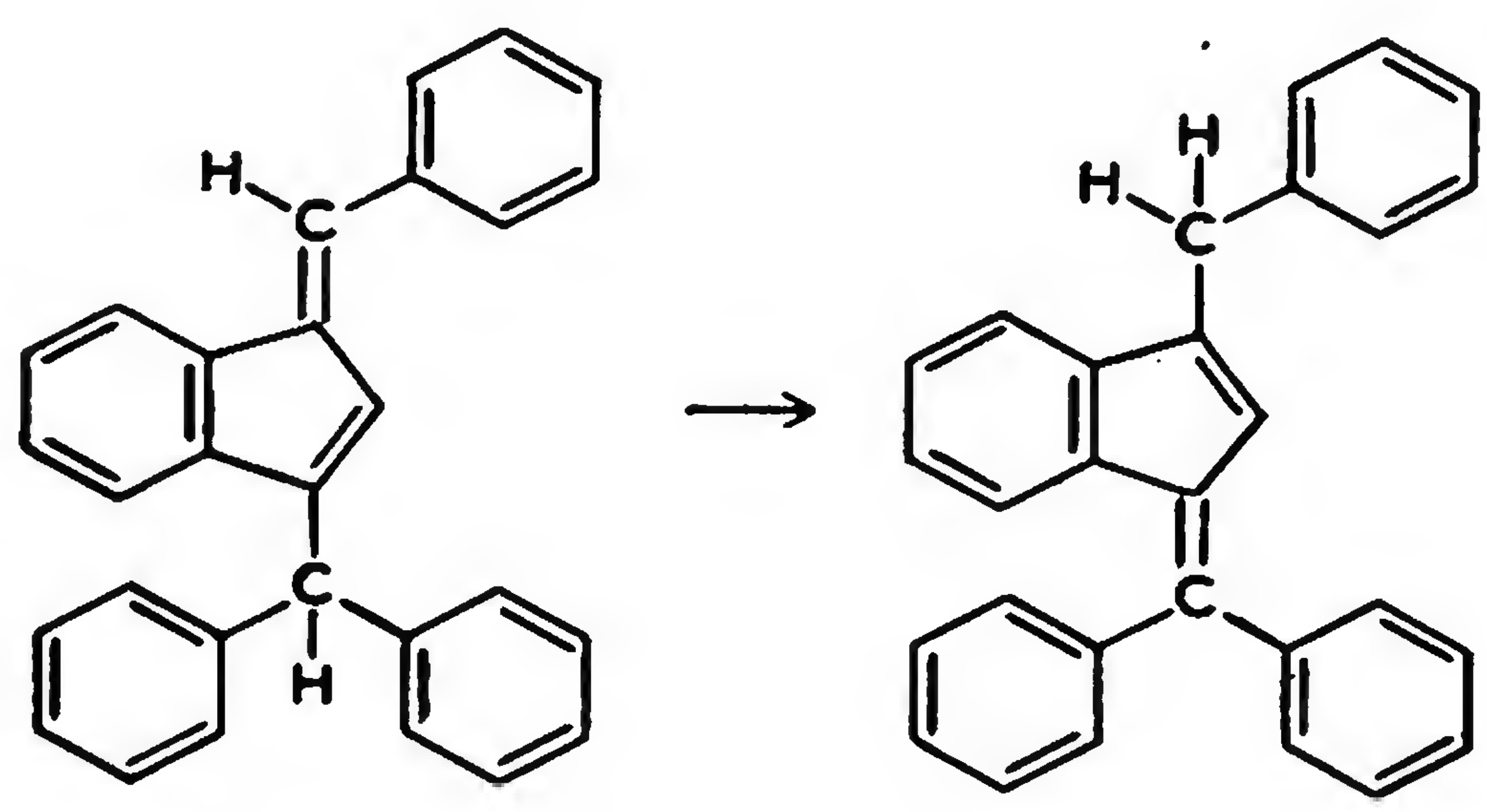
[m.p. 106-107°] [m.p. 98-100°]

[Mixture, m.p. 70°]

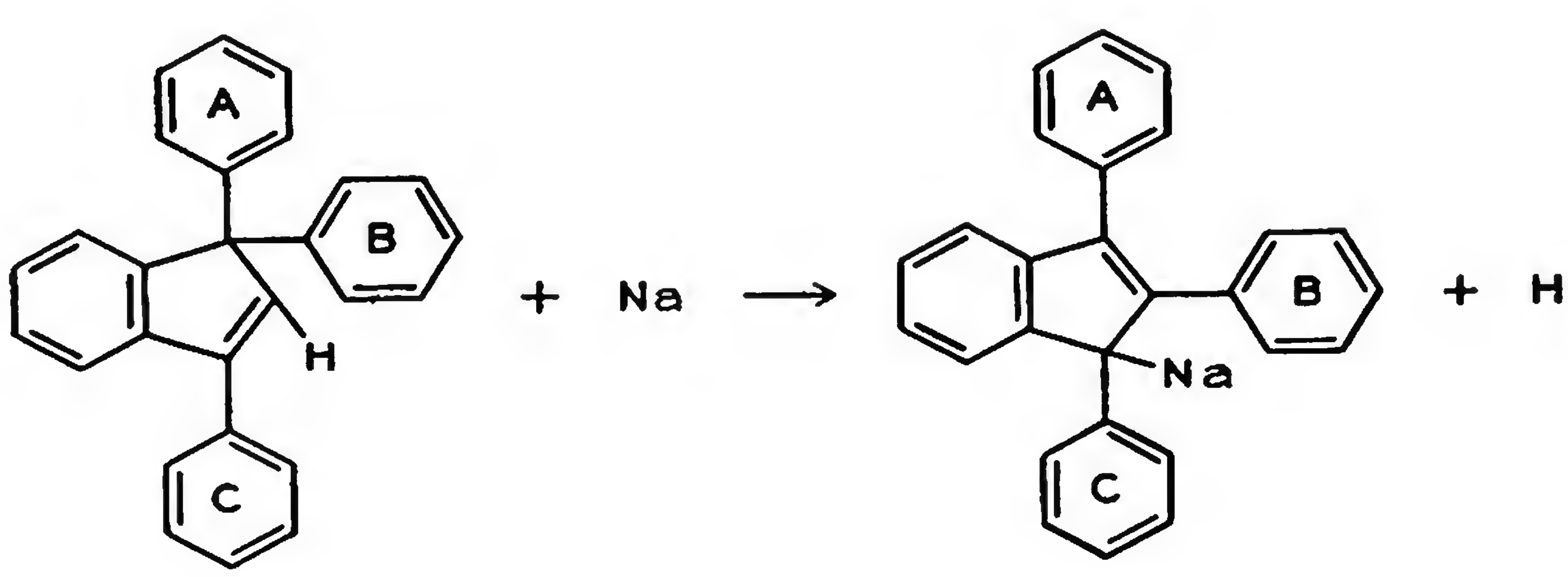


[m.p. 105-107°] [m.p. 93-94°]
[Mixture, m.p. 71-73°]

1-Benzylidene-3-benzhydryl-indene, boiled with potassium methoxide solution, formed 1-diphenylmethylene-3-benzylindene: [656]



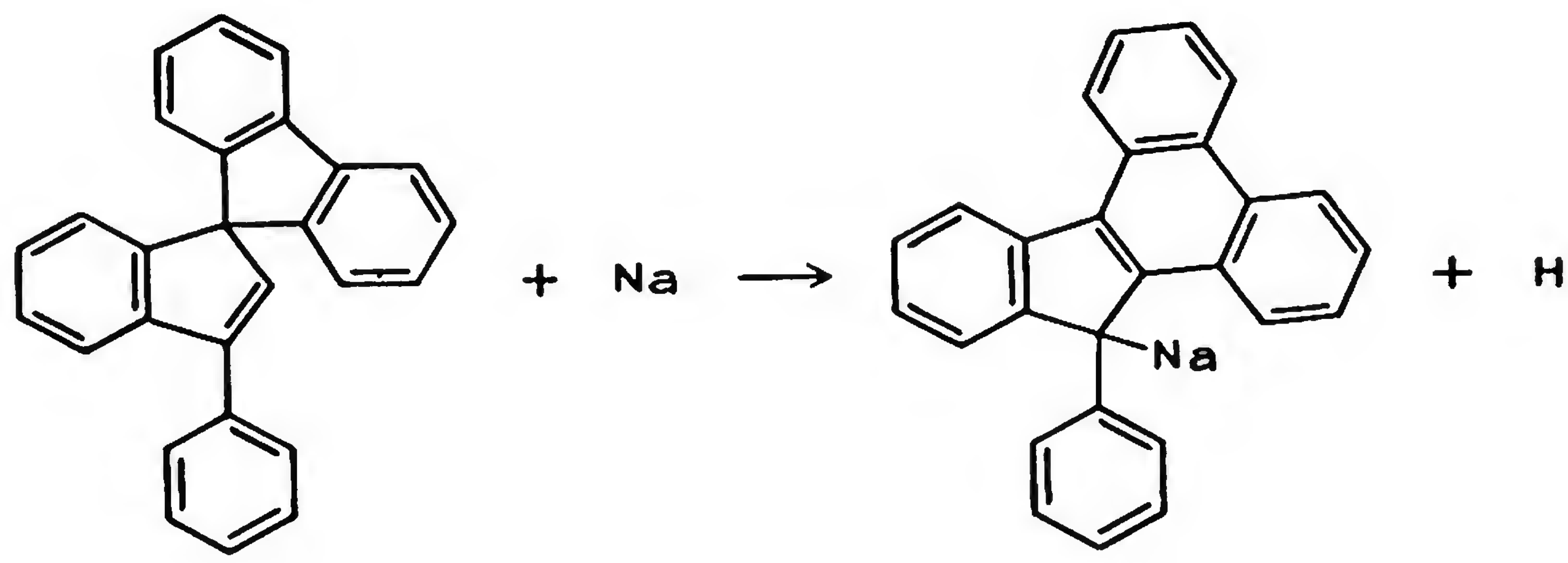
The treatment of 1,1,3-triphenylindene with sodium resulted in the migration of a phenyl group and in the formation of the sodium derivative of 1,2,3-triphenylindene: [678]



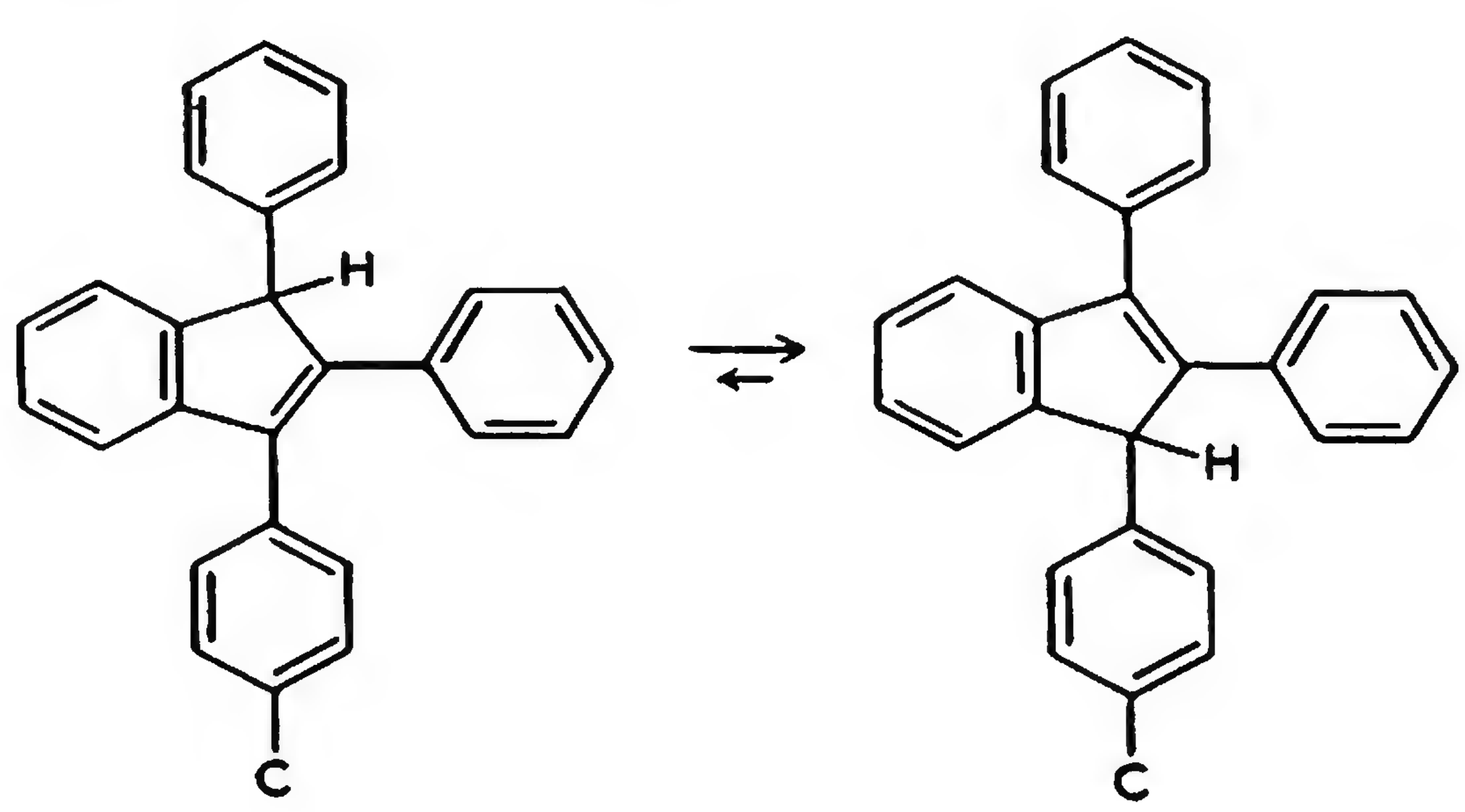
This, and some of the preceding reactions, are more complex than revealed by either their equations or the nomenclature of the hydrocarbons themselves. In view of the known behavior of indenes as a three-carbon system, it is desirable to write these equations with labeled phenyl groups, which would indicate double bond migrations.

1-Methyl-1,3,3-triphenylindane remained unchanged when heated at 215° for 6 days with "Floridin." [332] This hydrocarbon [332] was originally mistaken for 1,1,3,3-tetraphenylcyclobutane, but later investigations [54, 522] have rectified this error. It is of interest to compare at this point the less reactive indanes with the indenes.

1-Biphenylene-3-phenylindene and sodium gave the sodium derivative of 1,2,3,4-dibenzo-9-phenylfluorene.[313, 314] The sodium derivative, when acted upon by alcohol, forms the free hydrocarbon 1,2,3,4-dibenzo-9-phenylfluorene. The action of an excess of lithium on an ether solution of 1-biphenylene-3-phenylindene for 3 days also gave 1,2,3,4-dibenzo-9-phenylfluorene (80 per cent).[316] The course of these isomerizations is evident from the following equation:



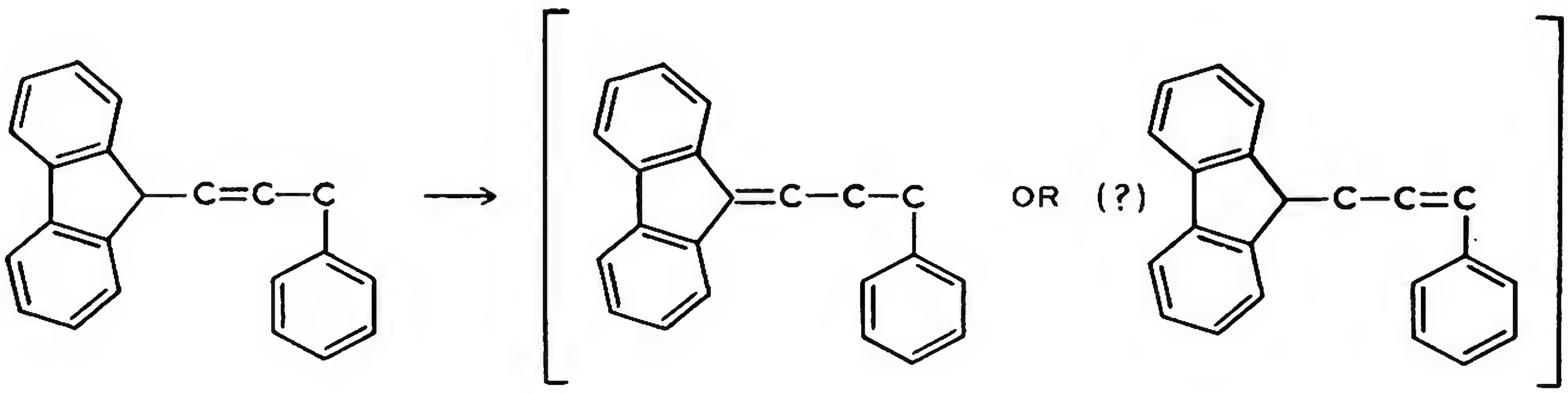
1,2-Diphenyl-3-*p*-tolylindene, boiled 1.25 hours with alcoholic potash, formed an equilibrium mixture of 1-*p*-tolyl-2,3-diphenylindene (90 per cent) and unchanged initial hydrocarbon (10 per cent).[315] Both 1,2-diphenyl-3-*p*-tolylindene and 1-*p*-tolyl-2,3-diphenylindene reacted with sodium amalgam in the presence of ether, forming sodium derivatives. Hydrolysis of the last compounds brought about the formation of practically the same mixture of indenes.[315] From this particular observation, the conclusion was drawn that the anion present is labile and that it is responsible for the occurrence of the equilibrium mixture. Moreover, it was probably correctly pointed out that the replacement of sodium by hydrogen immediately terminates the reaction at the equilibrium point established by the anions :



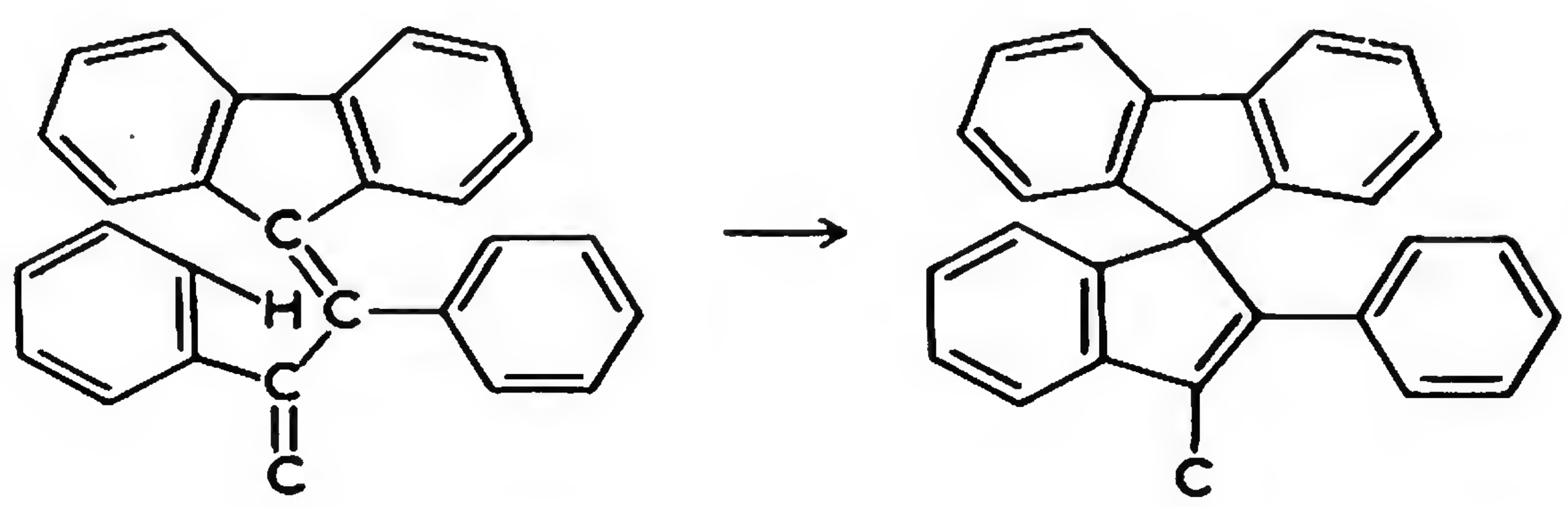
Fluorenes

1-Biphenylene-4-phenylbutene-2 (*i.e.*, "Δ^2 - dihydrocinnamylidene-fluorene"), when heated under reflux for 2 hours with sodium ethoxide solution, or when boiled for a long time with alcoholic piperidine, formed an isomer (m.p. 81-82°).[580] The new isomer was considered to be either

1-biphenylene - 4 - phenylbutene -1 (*i.e.,* "Δ^1 - dihydrocinnamylidenefluorene") or "possibly" 1-phenyl-4-biphenylenebutene-1 (*i.e.,* "Δ^3-dihydrocinnamylidenefluorene"):



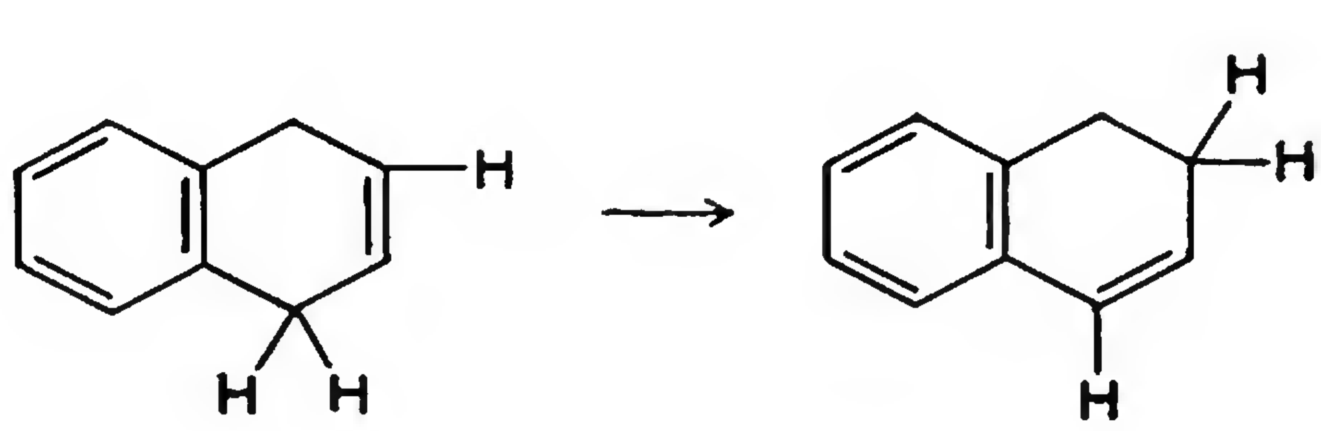
1-Biphenylene-2,3-diphenylbutadiene-1,3 was isomerized to 1-biphenylene-2-phenyl-3-methylindene (75 per cent) when boiled for an hour with acetic acid containing a small quantity of sulfuric acid.[316a] This cyclization involves an interesting 1:4 addition of a labile hydrogen atom from an ortho position:



Naphthalenes

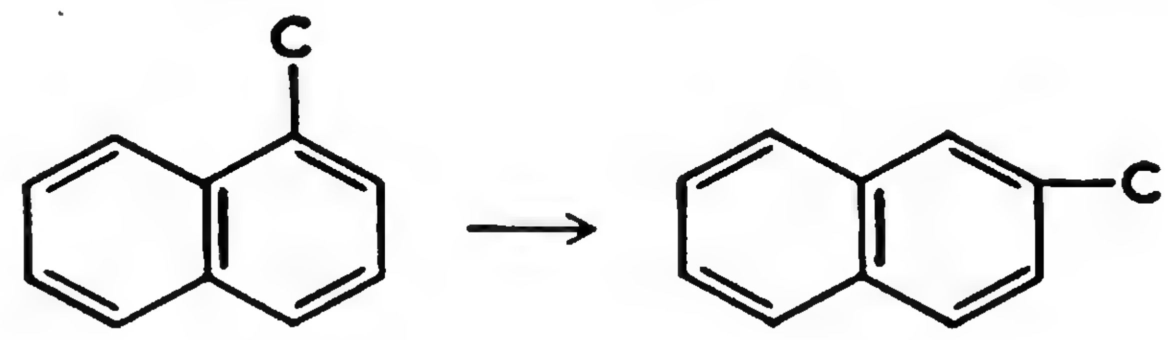
It is known that naphthalenes have a predisposition to change from 1-substituted into 2-substituted derivatives,[478] and that the latter are preferentially formed in the Friedel-Crafts reactions.

1,4-Dihydronaphthalene was isomerized to 1,2-dihydronaphthalene on heating at 100-105° [573] or at 150° [530] with a 10-per cent sodium ethoxide solution, or with a 5-per cent solution at 140-150°.[574] These isomerizations are in conformity with the substitution rule for naphthalenes, in spite of the presence of a cyclohexadiene ring, since a hydrogen atom migrates from 4-position into 2-position. The formation of 1,2-dihydronaphthalene corresponds to an allylic-type of isomerization:

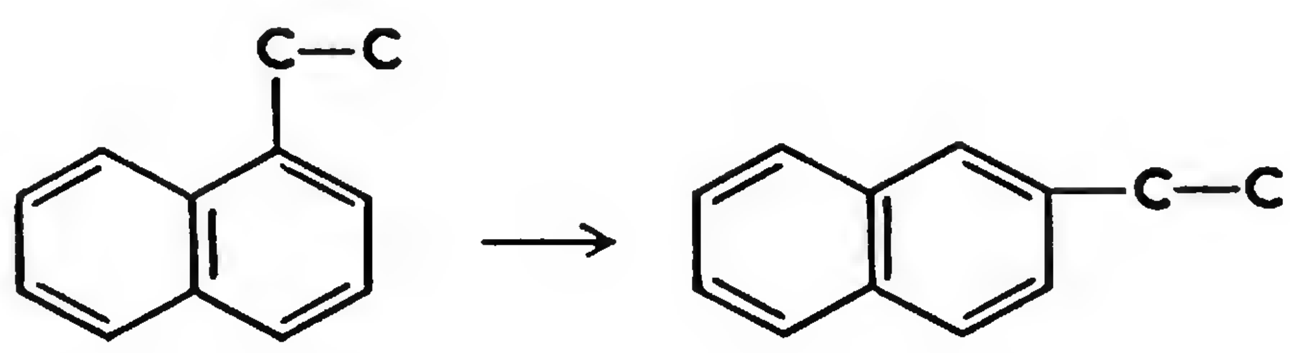


1,2-Dihydronaphthalene is 4.9 kilocalories per gram-mole more stable than 1,4-dihydronaphthalene.[184a, 575aa]

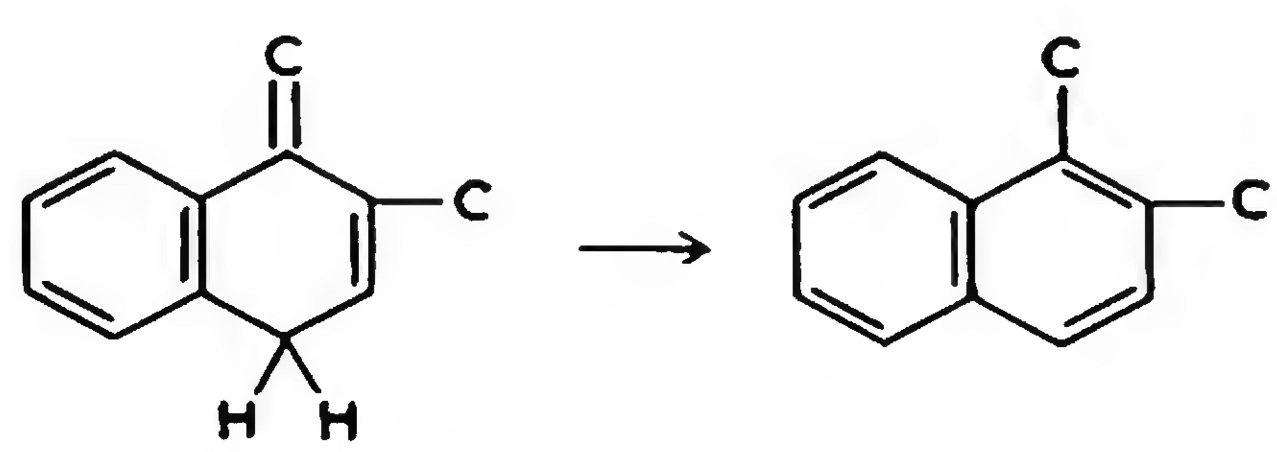
1-Methylnaphthalene, passed over silica gel at 420° in the presence of nitrogen, gave about 39 per cent of 2-methylnaphthalene: [365]



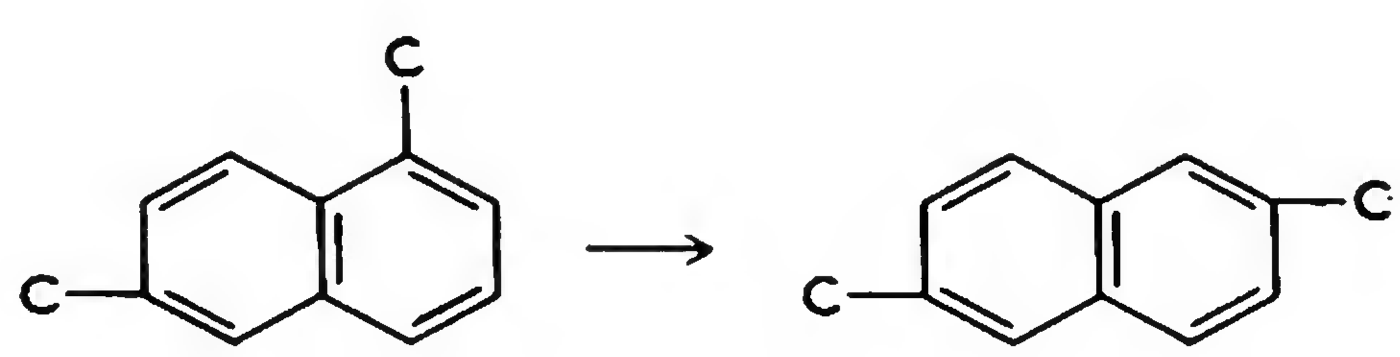
1-Ethylnaphthalene at 420-430° gave similarly 2-ethylnaphthalene: [365]



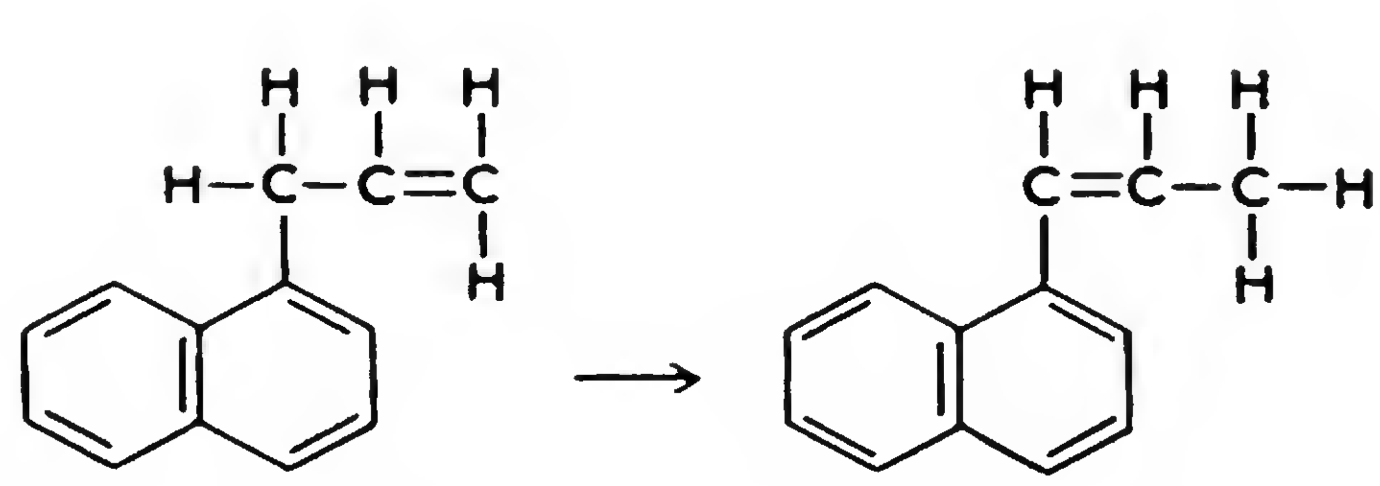
1-Methylene-2-methyl-1,4-dihydronaphthalene undergoes aromatization to 1,2-dimethylnaphthalene when boiled with acetic acid plus hydrogen chloride.[529] This reaction exemplifies a shift of a double bond into a ring under the influence of an acidic catalyst. Two double bonds move into new positions, as would be expected in the case of a five-carbon or "double allylic" system:



1,6-Dimethylnaphthalene when passed over silica gel at 400-420° gave 20 per cent of 2,6-dimethylnaphthalene and a considerable amount of the unchanged hydrocarbon: [365]

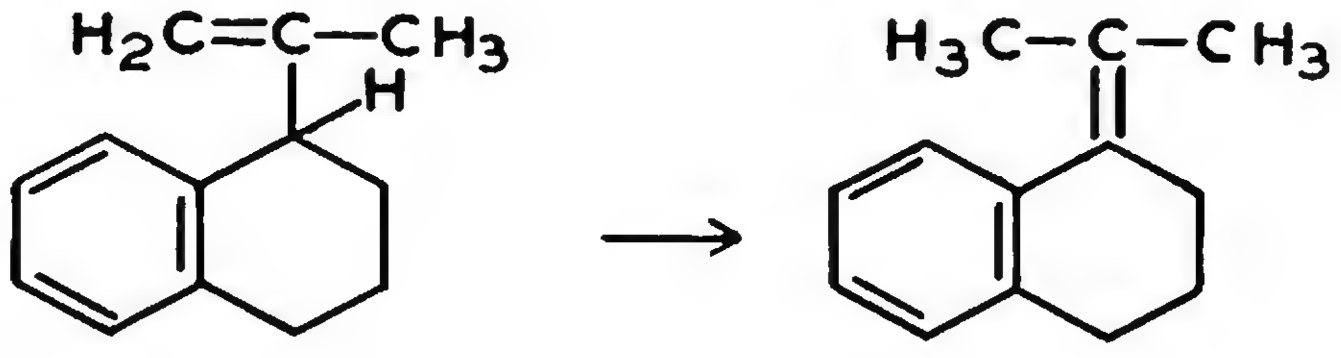


Passage of 1-allylnaphthalene through a tube filled with activated alumina at 500-550° and a pressure of 15 mm. Hg caused isomerization to 1-propenylnaphthalene.[185] A temperature of 300° is adequate for a slow isomerization over alumina.[342a] Boiling alcoholic potash effects the same reaction: [585]



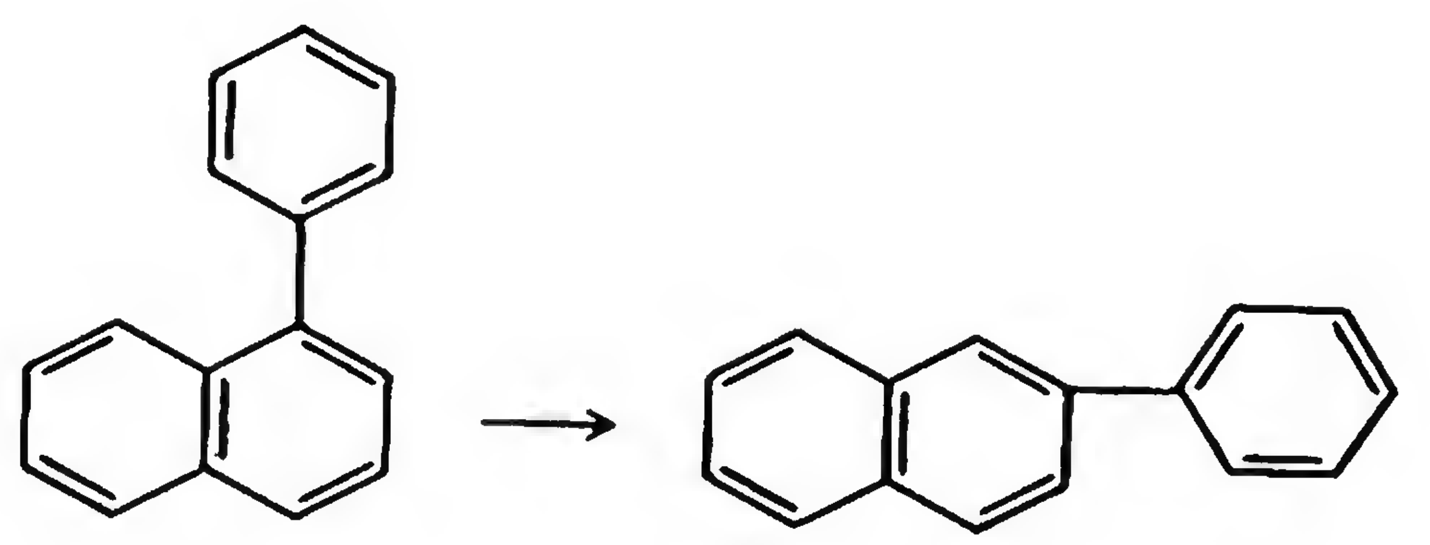
1-Isopropenyl-1,2,3,4-tetrahydronaphthalene isomerizes to at least 75 per cent of 1-isopropylidene-1,2,3,4-tetrahydronaphthalene upon being

heated with sodium ethoxide solution.[299] This high yield is to be expected on account of the alkaline catalyst, which causes an arrest of the double bond at the ring position:

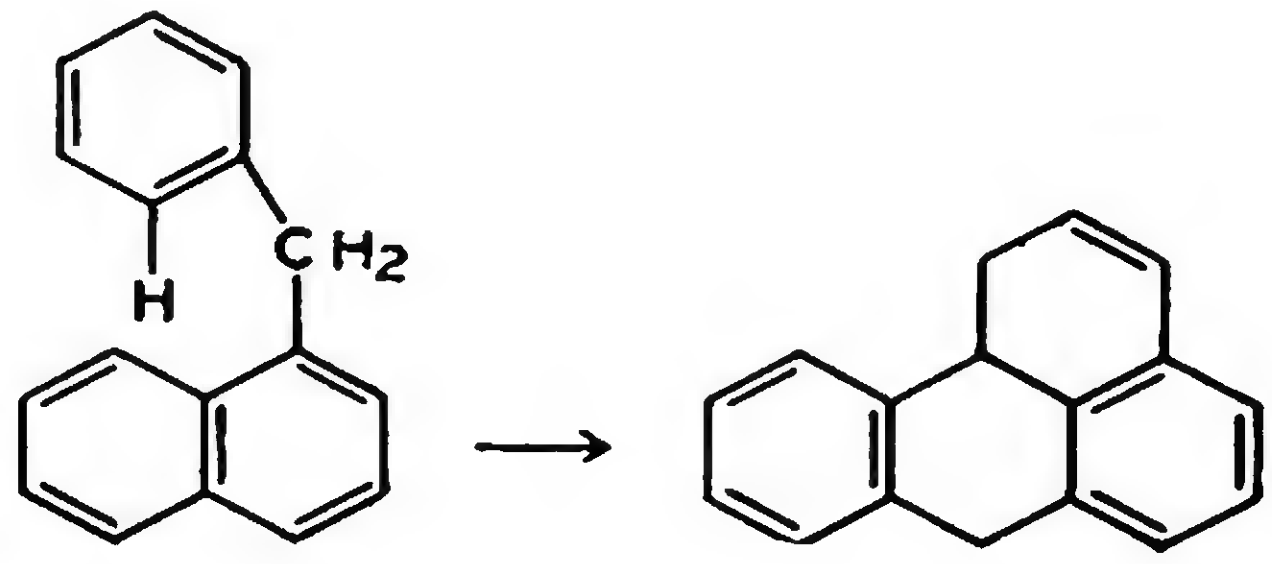


The reaction is related to the limonene-terpinolene isomerization, having the same type of hydrogen migration.

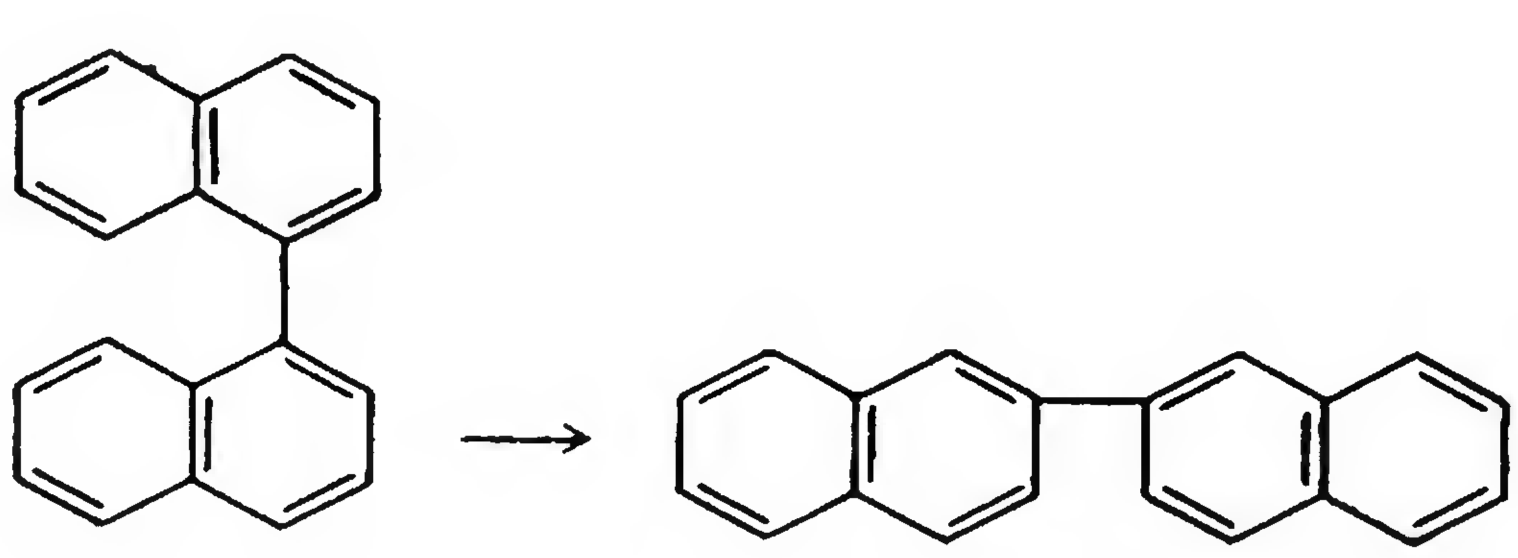
1-Phenylnaphthalene was isomerized to 2-phenylnaphthalene at 350° in the presence of silica gel, cobalt silicate, and copper silicate as catalysts, using either air or hydrogen as the vapor carrier: [365]



1-Benzylnaphthalene isomerized to 1,11b-dihydro-7 - benz[de]-anthrene upon passage through an empty "glowing" tube,[225] or through one containing pumice.[525] The product at first was assumed to be $C_{17}H_{12}$ or "isochrysofluorene." [225] Later work,[525] determined its true composition, $C_{17}H_{14}$, which corresponds to a "dihydrobenzanthrene." The reaction can be considered as an intramolecular alkylation requiring the closure of phenyl and hydrogen upon an active double bond within the naphthalene ring:

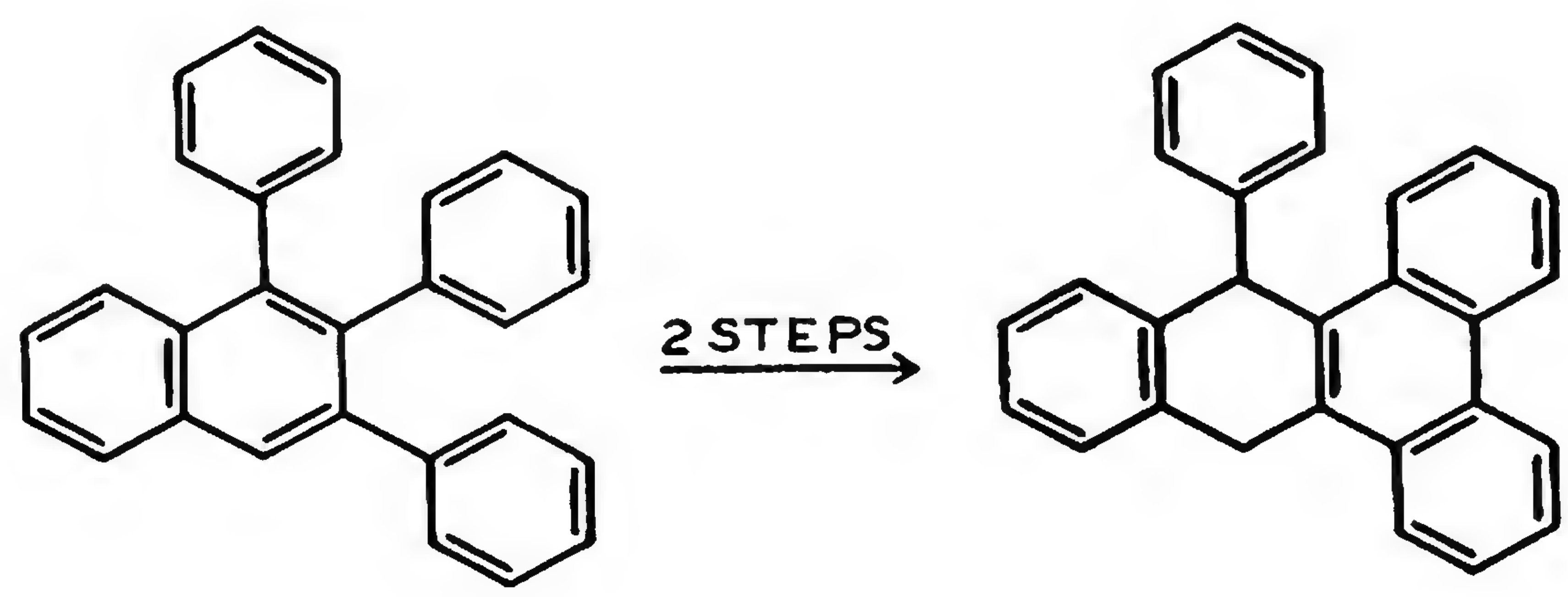


1,1′-Dinaphthyl, heated with aluminum chloride in the presence of carbon disulfide, forms some 2,2′-dinaphthyl: [526]



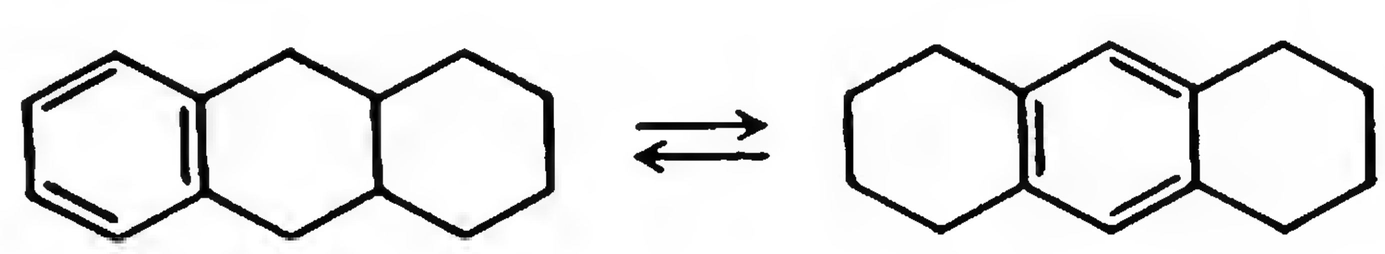
This isomerization is similar to that of 1-phenylnaphthalene.

1,2,3-Triphenylnaphthalene, agitated with lithium for 8 days in ether solution, yielded a colored precipitate. The latter formed 9-phenyl-9,14-dihydro-dibenz[ac]anthracene (*i.e.*, 9-phenyl-9,10-dihydro-1,2,3,4-dibenz-anthracene) upon contact with alcohol: [57a]



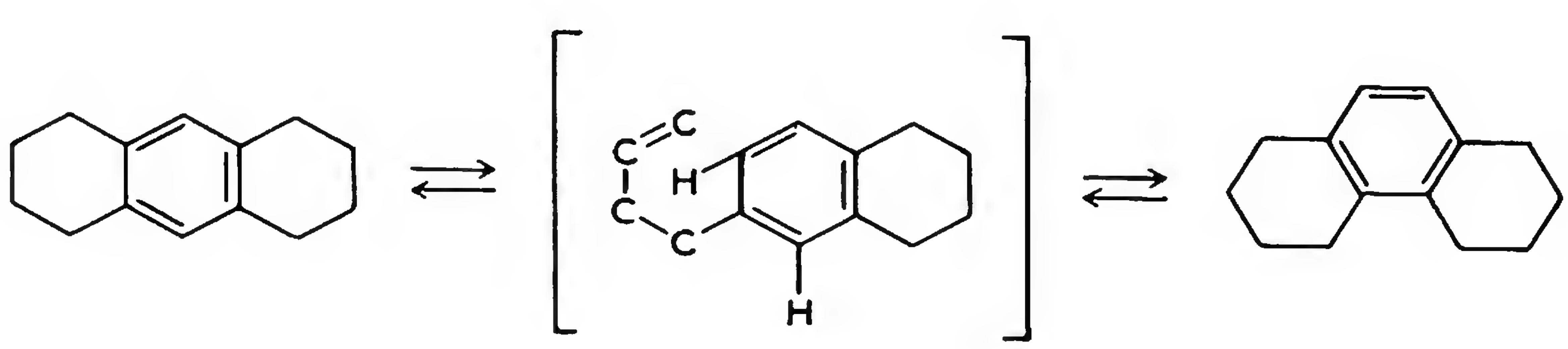
Anthracenes

1,2,3,4,4a,9,9a,10- and 1,2,3,4,5,6,7,8-Octahydroanthracenes undergo an interconversion, or extensive dehydrogenation plus hydrogenation, when heated at 340-370° and 335°, respectively, for several hours at 100 atmospheres' hydrogen pressure with molybdenum disulfide as catalyst.[450] Since yields were not reported, it is impossible to state which isomer is the more stable. The interconversion of these unsymmetrical and symmetrical octahydroanthracenes indicates that at least two of the three double bonds within an aromatic ring can shift into an attached fused-ring:



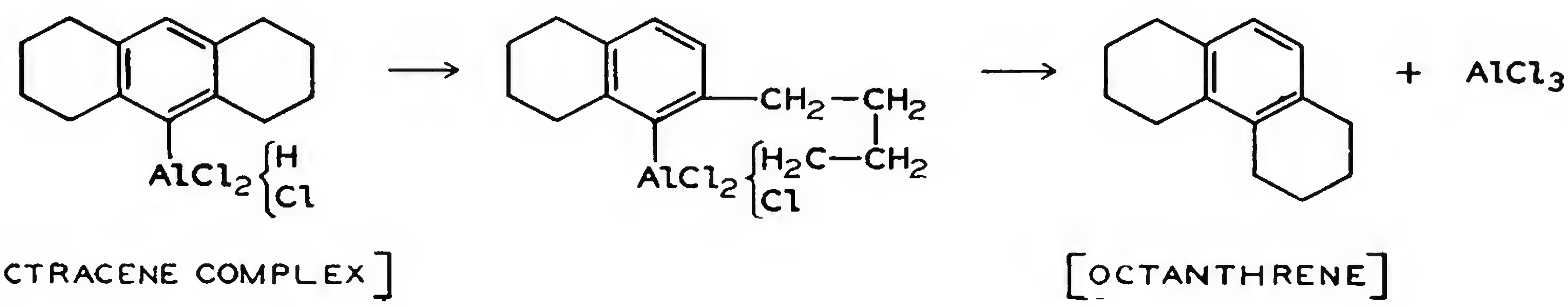
[UNSYM.] [SYM.]

However, 1,2,3,4,5,6,7,8-octahydroanthracene, when treated similarly with molybdenum disulfide at the higher temperature point of 390°, yielded 34.25 per cent of 1,2,3,4,5,6,7,8-octahydrophenanthrene.[453] The presence of the last product can be explained by assuming (a) the formation of 1,2,3,4-tetrahydro-6-(3-butenyl)naphthalene as an intermediate and (b) the acquisition of a labile hydrogen at the phenanthrene "6" position by removal from the anthracene "10" position. This would be an example of a simple dealkylation plus alkylation in a condensed ring system:

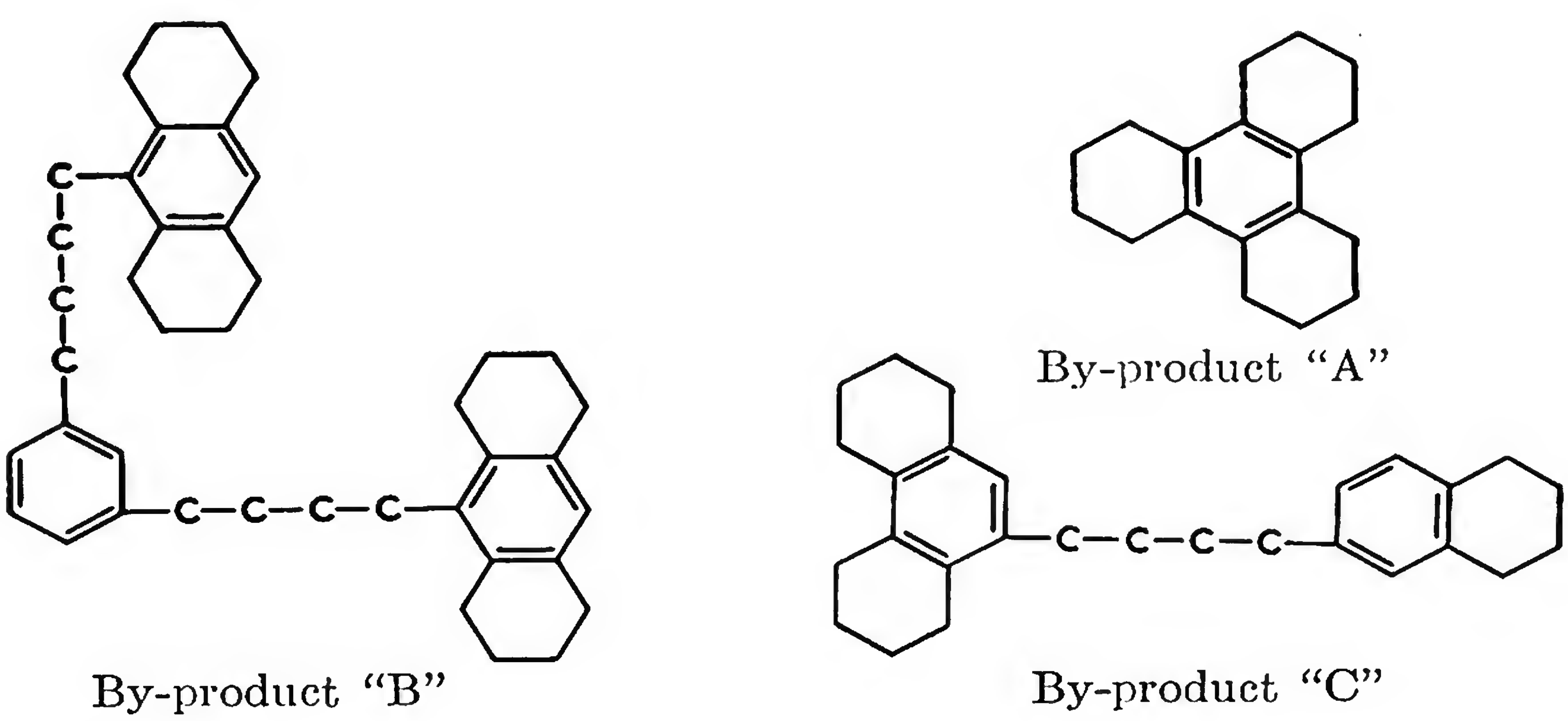


In the next section, under "Phenanthrenes," it is shown that this isomerization is reversible when aluminum chloride is used as catalyst. 1,2,3,-4,5,6,7,8-Octahydroanthracene, heated with aluminum chloride at 70-80°,

yielded 40-44 per cent of 1,2,3,4,5,6,7,8-octahydrophenanthrene (*i.e.*, octanthrene), together with 44 per cent of the starting hydrocarbon, 4.4-4.8 per cent of dodecahydrotriphenylene (*i.e.*, "A"), 4.0 per cent of a combined fraction of "phenylene-bis-octracenylbutane" [this may be "B," *i.e.*, 1,3-bis-(4-[9-octracenyl]-butyl)benzene] and "tetralyl-octanthrenyl-butane" [which may be "C," *i.e.*, 6-(4-[9-octanthrenyl]butyl)-1,-2,3,4-tetrahydronaphthalene], and a small amount of a yellow hydrocarbon (m.p. 320°).[528] This reaction was interpreted by assuming the preliminary formation of an octracenyl-aluminum chloride-hydrochloride:[528]



The by-products "A," "B," and "C," are in support of this assumption:

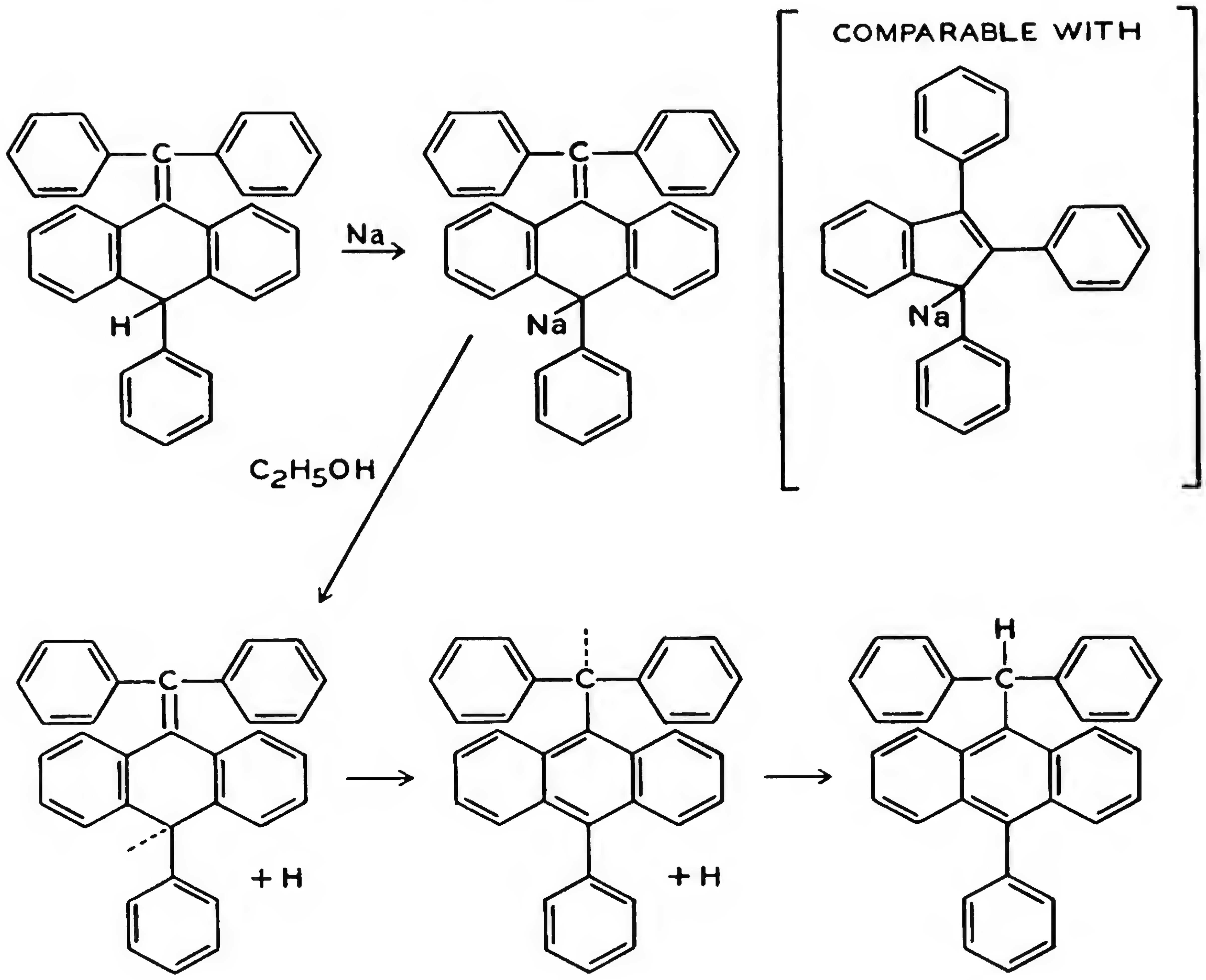


By-product "A"

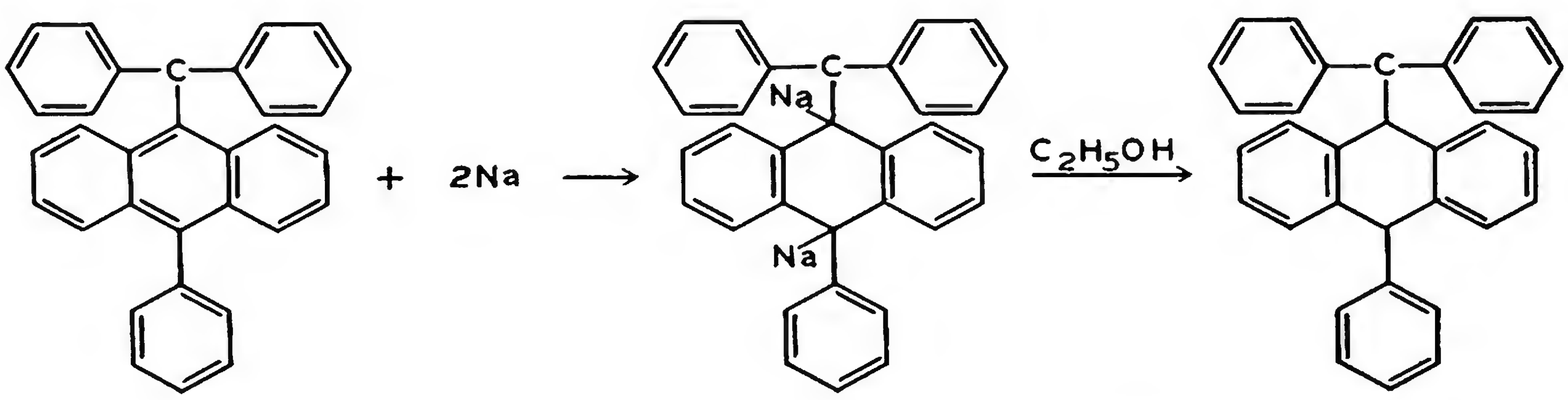
By-product "B"

By-product "C"

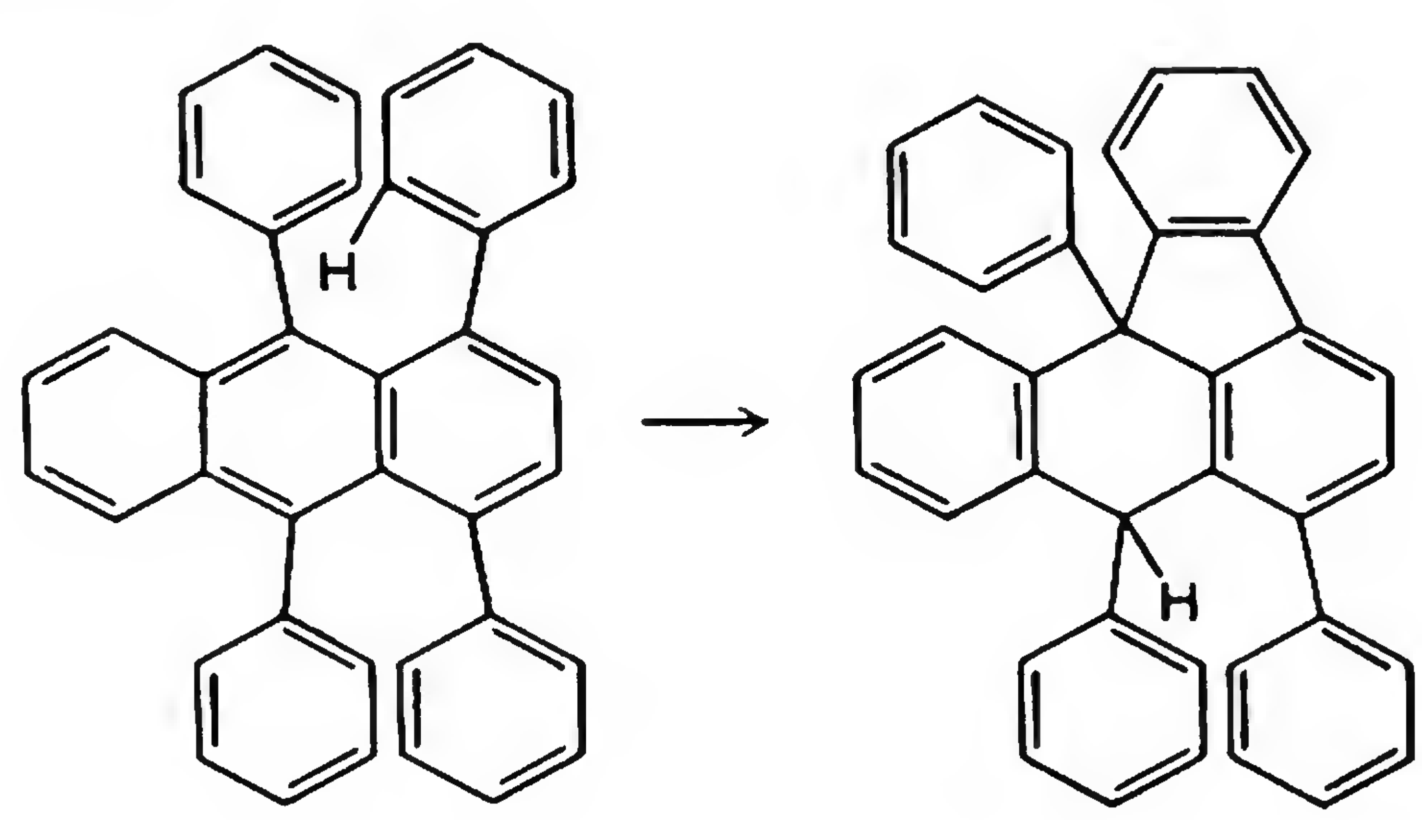
9-Benzohydrylidene-10-phenyl-9,10-dihydroanthracene, agitated with sodium for 8 days in ether solution, gave a dark-red coloration, due to formation of a monosodium substitution product. Treatment of the scarlet-red precipitate of the organosodium product (obtainable after 10 weeks of shaking in the presence of sodium), with alcohol, led to the formation of 9-benzohydryl-10-phenylanthracene.[44] The structure of the monosodium derivative of 9-benzohydrylidene-10-phenyl-9,10-dihydroanthracene was considered by the experimenter to be analogous to that of the sodium derivative of 1,2,3-triphenylindene. Hydrolysis probably led to the formation of the corresponding free radical, which then isomerized to another free radical related directly to 9-benzyohydryl-10-phenylanthracene:



The foregoing metalation plus demetalation is irreversible. 9-Benzohydryl-10-phenylanthracene gave a blue-violet coloration when agitated with sodium powder for 8 days in ether solution, due to the formation of a disodium addition product.[44] Treatment of the resulting solution with alcohol, and thereafter with water, gave 9-benzhydryl-10-phenyl-9,10-dihydroanthracene:

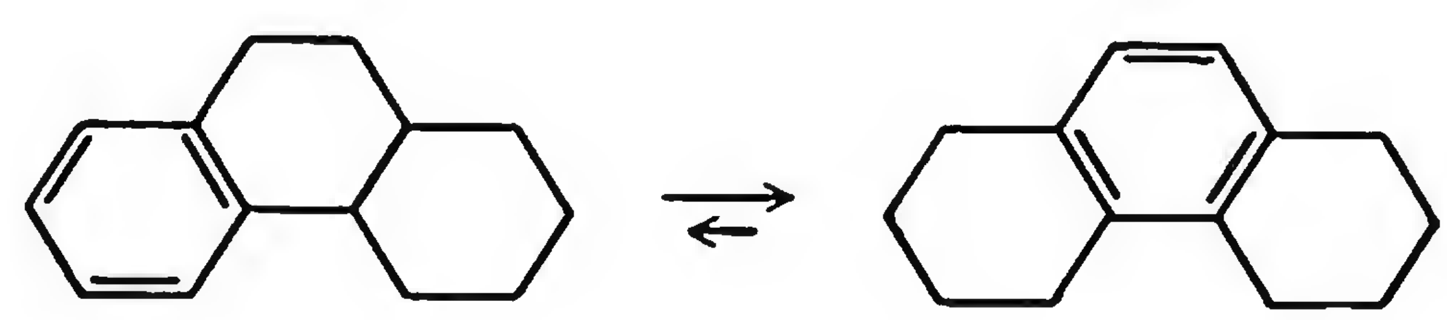


1,4,9,10-Tetraphenylanthracene, when heated under reflux with an excess of formic acid, formed 4,9,10-triphenyl-1,9-(*o*-phenylene)-9,10-dihydroanthracene: [640]



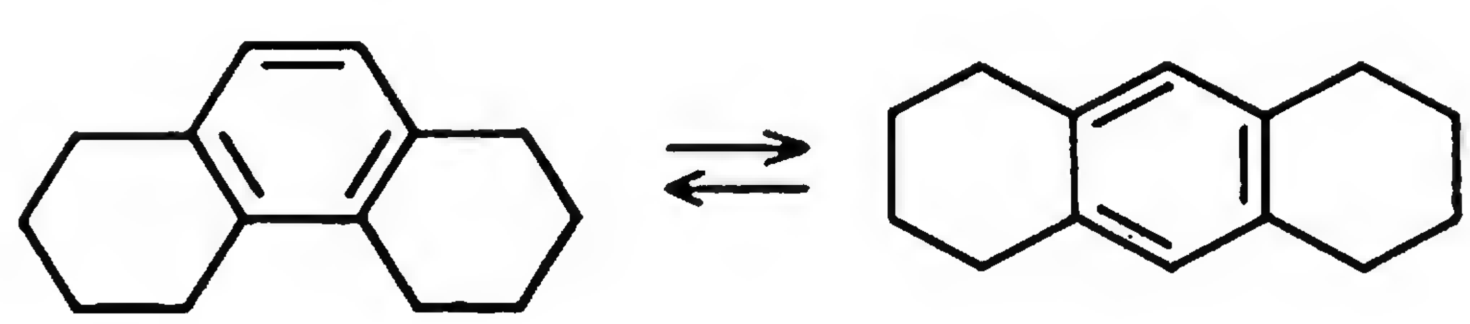
Phenanthrenes

1,2,3,4,4a,9,10,10a- and 1,2,3,4,5,6,7,8-Octahydrophenanthrenes (5-31 g.) undergo an interconversion, or dehydrogenation plus hydrogenation, when heated at 130° for 2-10 hours in a steel bomb at 100-140 atmospheres' pressure of nitrogen with Raney's nickel (2-3 g.), or at temperatures 50-100° higher with copper-chromium oxide (2-4 g.).[150] Since only 3-4 per cent of unsym-octahydrophenanthrene formed, the symmetrical octahydrophenanthrene is the more stable isomer. The former gave at least 15 per cent of the latter after 5 hours of treatment, and 28 per cent after 19 hours. The interconversion of these isomers confirms the observation that at least two of the three double bonds within an aromatic ring can shift into an attached fused-ring:

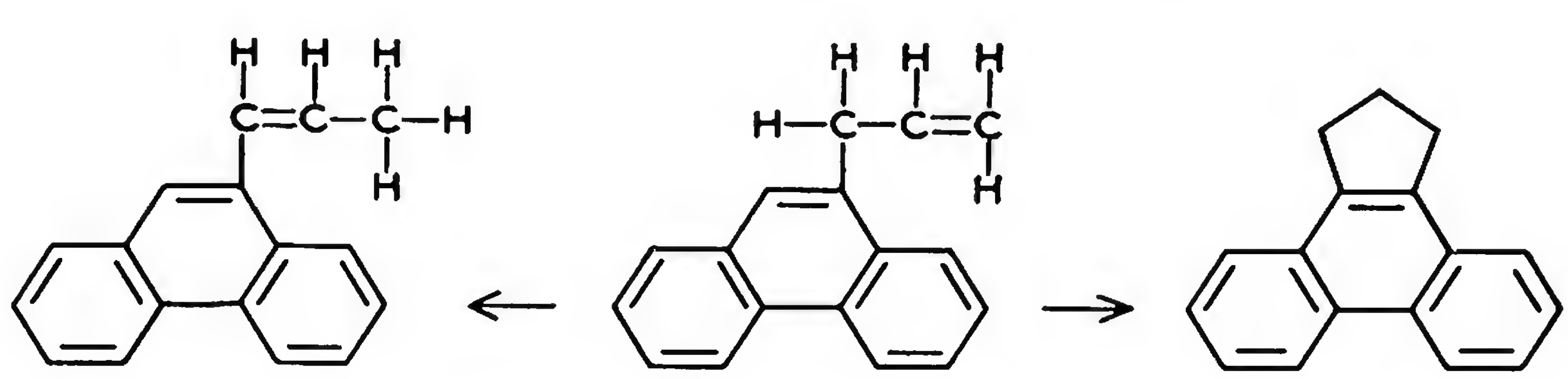


[UNSYM.] [SYM.]

1,2,3,4,5,6,7,8-Octahydrophenanthrene (*i.e.*, octanthrene) can undergo also an isomerization into 1,2,3,4,5,6,7,8-octahydroanthracene (*i.e.*, octracene). Heated with aluminum chloride at 80°, the former gave a mixture of octanthrene and octracene (45 per cent of each), together with dodecahydrotriphenylene (10 per cent) and other hydrocarbons: [528]

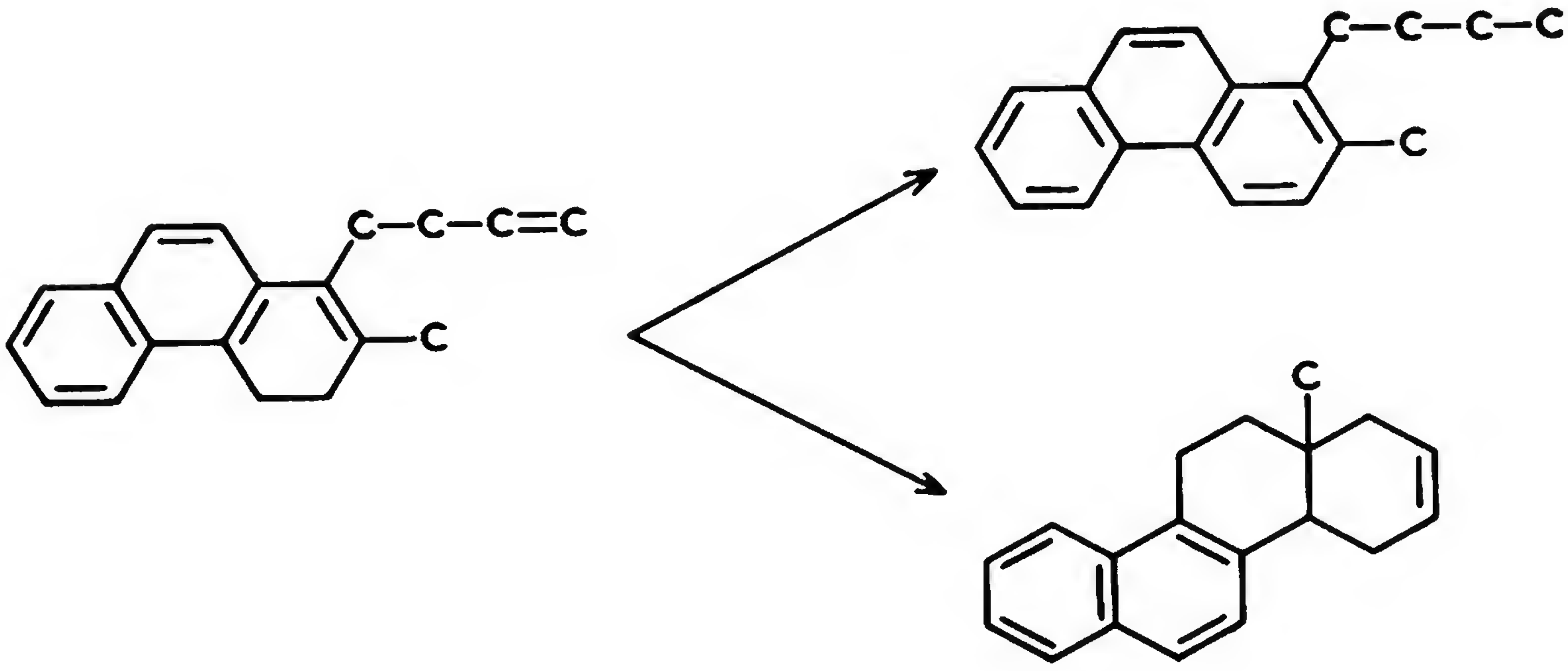


9-Allylphenanthrene isomerized to 9-propenylphenanthrene upon boiling with alcoholic potash for 4 hours,[47] but gave 2,3-dihydro-1-cyclopenta[*l*]phenanthrene (*i.e.*, 9,10-cyclopentenophenanthrene) when treated with excess of lithium (in ether), then with alcohol to hydrolyze a mono-substitution product (lithium at the α-position on allyl), and thereafter separated from some regenerated 9-allylphenanthrene: [58]



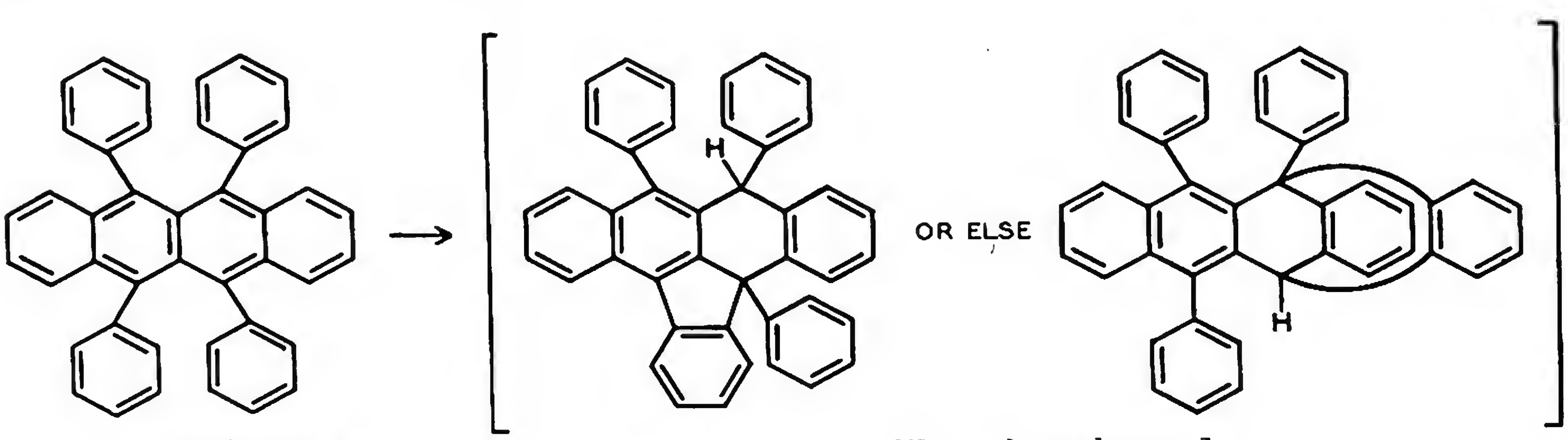
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene yielded 1-butyl-2-methylphenanthrene when heated successively at 260-265° and 280-285°

with palladinized charcoal.[95a] Treatments with phosphorus pentoxide at 140° or 170°, or else with acetic acid plus phosphoric acid at 100°, led to the formation of a methylhexahydrochrysene, presumably 12a-methyl-1,4,4a,11,12,12a-hexahydrochrysene: [95a]



Naphthacenes

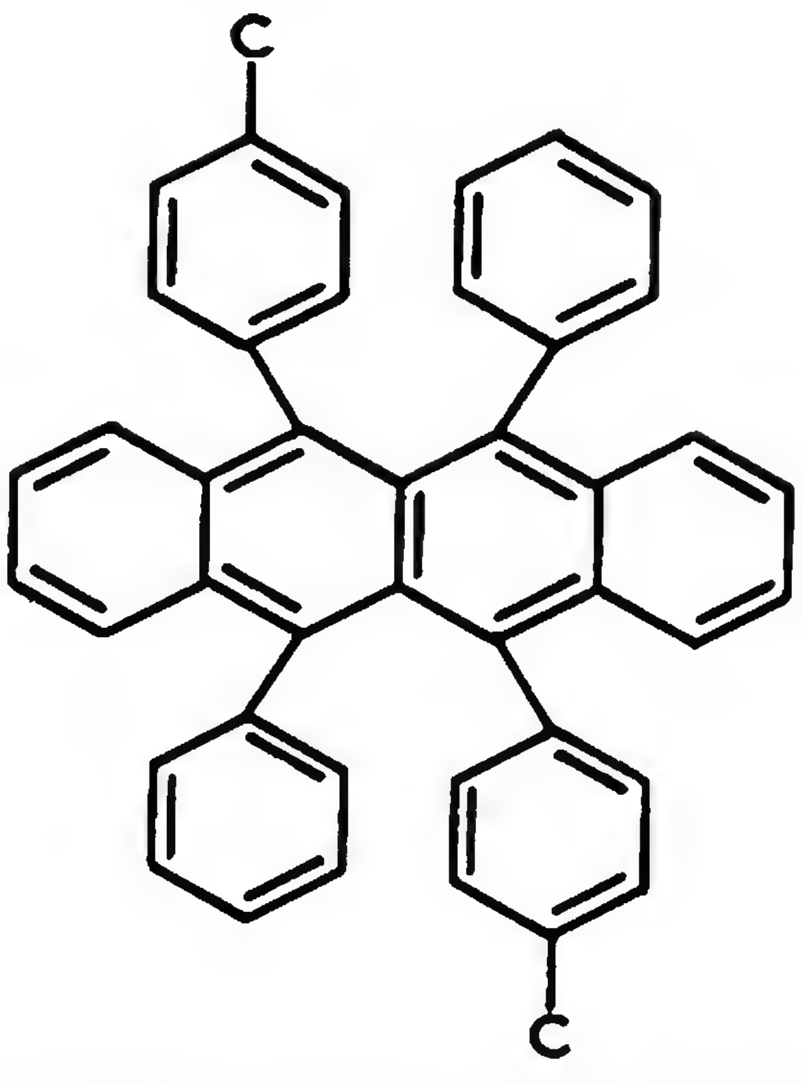
The action of gaseous hydrogen iodide upon solutions of 5,6,11,12-tetraphenylnaphthacene (*i.e.*, rubrene) yielded an isomer (pseudo-rubrene) and reduction products.[34, 143, 387, 388] Two structures have been proposed for pseudo-rubrene.[142] One of the proposed structures, that of 5,11,12-triphenyl-5,6-(*o* - phenylene) - 5,12 - dihydronaphthacene, seems preferable to the other: [640]



[Rubrene] [Pseudo-rubrene]

Reduction of rubrene by gaseous hydrogen iodide dissolved in ether gives two colorless "dihydrorubrenes" (m.p. 230-231° and 249-250°). The higher-melting compound is capable of isomerization into the lower-melting product when heated with sodium isoamylate solution.[143] These "dihydrorubrenes" seem to be quite different from the yellow isomers ($C_{42}H_{30}$) via isomerization of 1,3,3,4,4,6-hexaphenylhexadiyne-1,5, encountered in the section of "Alkynyl Benzenes." Hence, the colorless "dihydrorubrenes" can be considered as dihydronaphthacenes, more or less "phenylenated."

Treatment of a benzene solution of dimethylrubrene with a strong acid, such as sulfuric acid, gave two isomers that are difficult to separate and which have melting points of 271-272° and 293-294°, respectively.[165]



Probable Structure of Dimethylrubrene

Isomerizations of the condensed aromatics are listed systematically in Table 40,* p. 384.

Conclusions

1. Indanes with unsaturated side-chains isomerize into indenes under thermal conditions or in the presence of acidic catalysts.

2. Isomerizations observed in the group of simpler indenes include: (a) an allylic type of hydrogen migration, (b) redistributions of aryl groups, (c) cyclizations, and (d) *endo-exo* oscillation of two conjugated double bonds.

3. Fluorene derivatives undergo changes in unsaturated side-chains. One fluorene isomerizes in the manner of butene-2 into butene-1. Another fluorene, with a side-chain containing two double bonds and phenyl groups, undergoes a cyclization to an indene with a biphenylene side-chain.

4. Isomerizations of naphthalenes include: (a) several allylic types of hydrogen migration in ring and side-chain, (b) redistributions of alkyl and aryl groups, (c) cyclizations, and (d) "aromatization."

5. Anthracenes isomerize by hydrogen migration. The latter caused: (a) the cyclization of an "unhydrogenated" polyaryl anthracene, (b) decyclization plus cyclization within an octahydrogenated anthracene, with development of a new ring system, and (c) the stabilization of liquid "perhydrogenated" anthracene by the formation of a solid form. This series of isomerizations indicates a relationship between cyclization and the degree of unsaturation of these molecules.

6. Phenanthrenes isomerize by: (a) hydrogen migration within ring and side-chain or from ring to side-chain (aromatization), (b) cyclization, and (c) decyclization plus recyclization.

* This table lacks a few examples given in Tables 41 and 42.

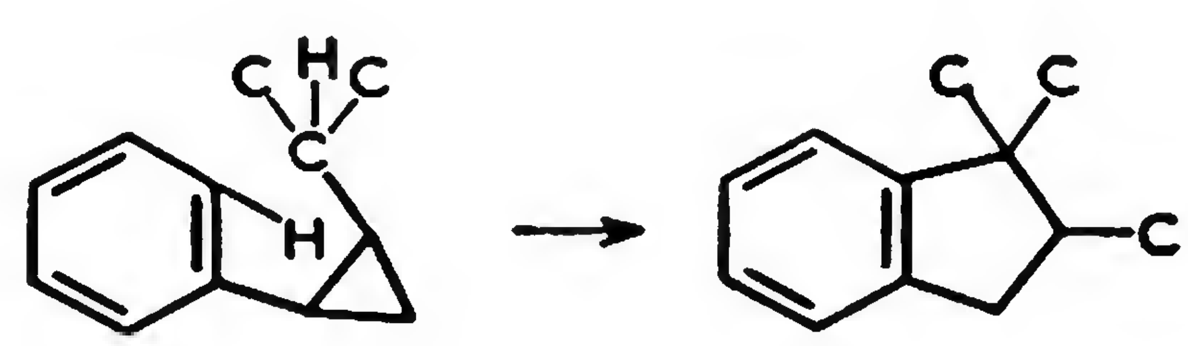
7. Rubrenes and hydrorubrenes, which are highly condensed aromatics or naphthacenes, probably isomerize by cyclization involving *o*-phenylenation.

Aromatic-Cyclane Hydrocarbons

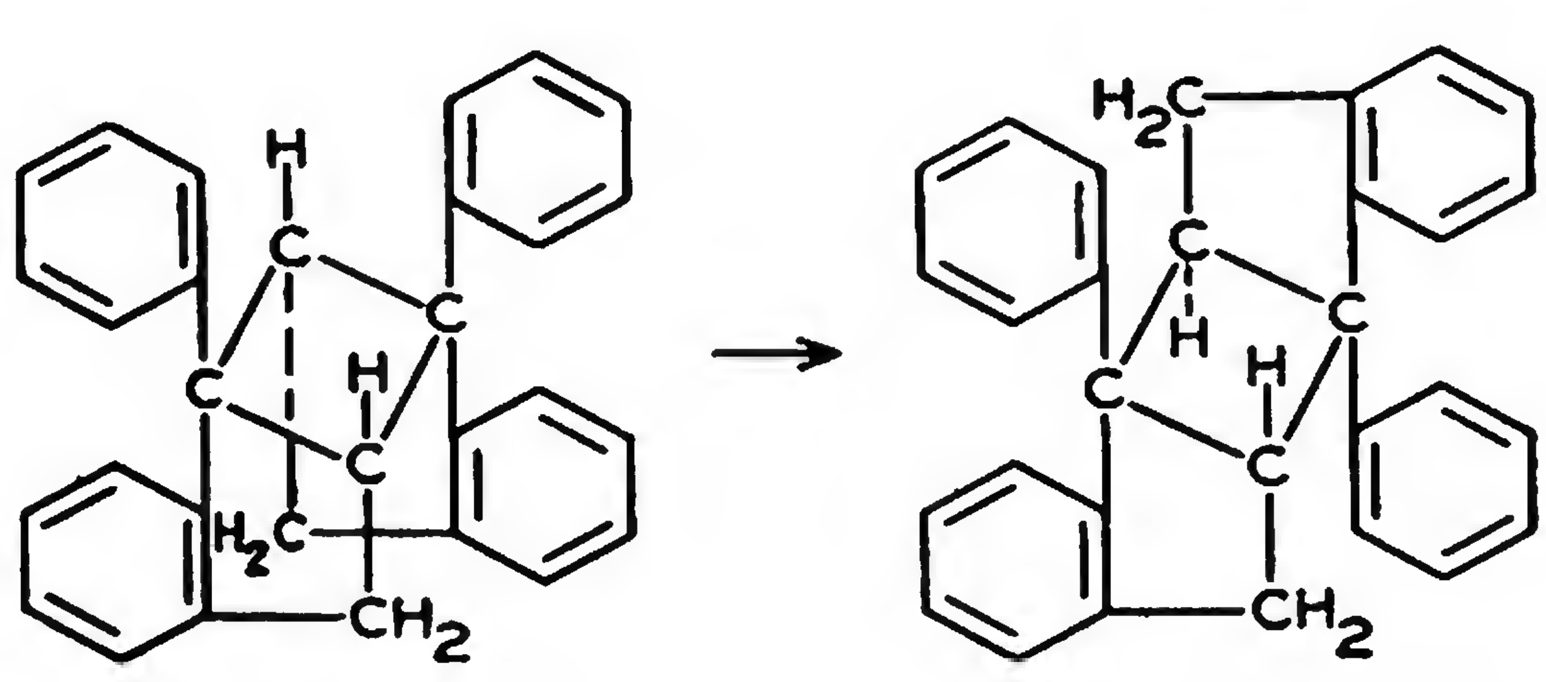
Only a few examples of isomerization are known in the group of cyclanes containing phenyl groups. This is indicative partly of the stable structures usually assigned to cyclanes and to the benzene ring. These isomerizations are considered in order of increasing size of the cyclane ring.

Isomerizations

1-Isopropyl-2-phenylcyclopropane, treated with 90-per cent sulfuric acid, selectively opens up the cyclopropane ring at one point and forms 1,1,2-trimethylindane.[131a] This isomerization involves the transfer of two hydrogen atoms:



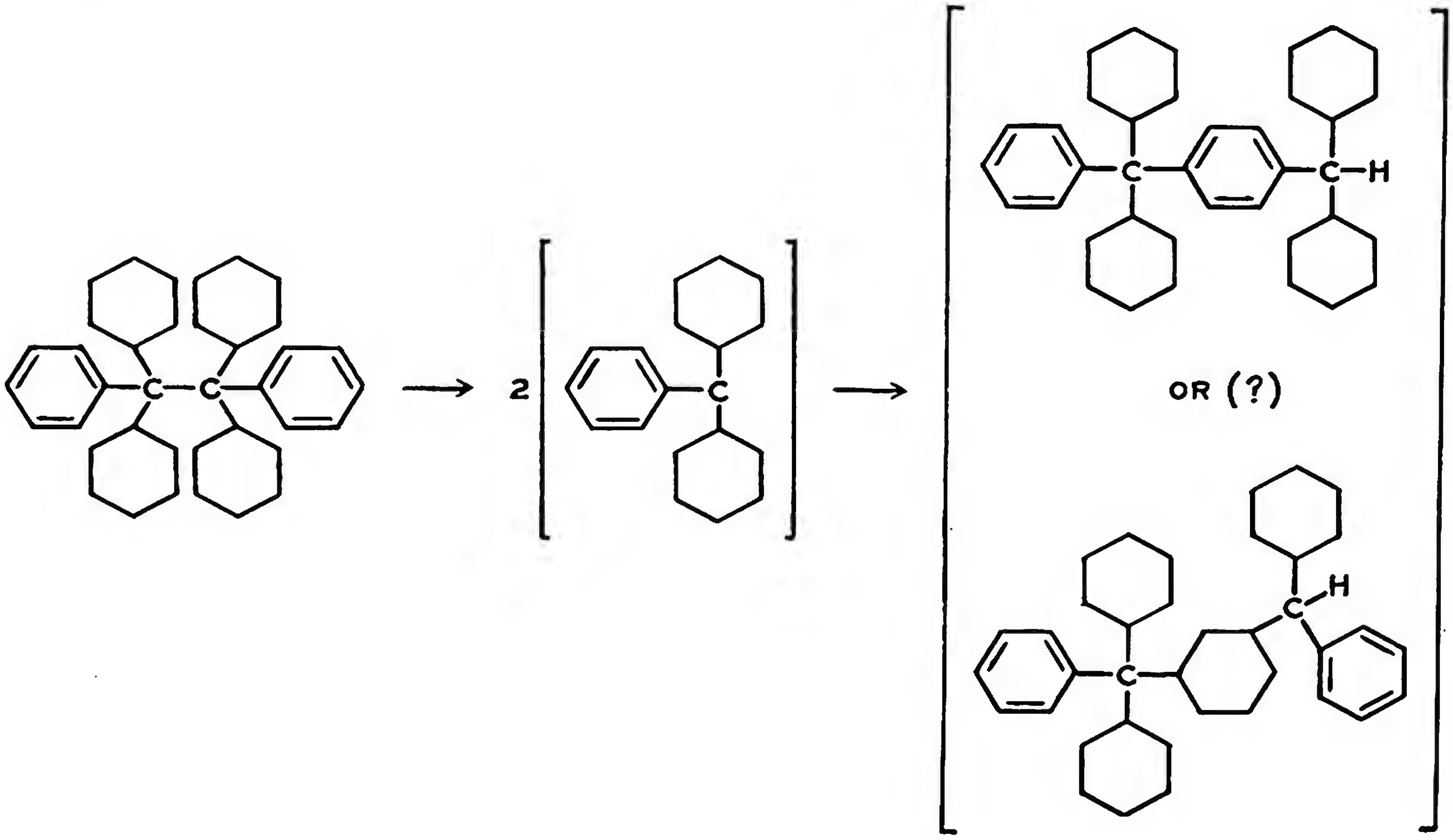
"γ-Diphenyl-truxane," which may be considered both as a "condensed 1,3-dialkyl-2,2,4,4-tetraaryl-cyclobutane" and as a *cis*-diphenyl-*cis*-di-*o*-benzylene-cyclobutane, was isomerized completely when heated at a temperature somewhat above its melting point for 5 hours.[568] The product of isomerization is "α-diphenyl-truxane," *i.e.*, the corresponding *trans*-diphenyl-*trans*-di-*o*-benzylene-cyclobutane:



$2^c,4^c$-Diphenyl-$1^t(CH_2),2^t$—$3^t(CH_2),4^t$-di-*o*-benzylene-cyclobutane "γ-Diphenyl-truxane"	$2^t,4^c$-Diphenyl-$1^c(CH_2),2^c$—$3^t(CH_2),4^t$-di-*o*-benzylene-cyclobutane "α-Diphenyl-truxane"

1,2,4-Triphenylcyclopentane exists in a metastable liquid form that changes very slowly into a stable solid, which probably is a geometrical isomer.[403] 1-Methyl-2,3,5-triphenylcyclopentane and 1,3-dimethyl-2,4,5-triphenylcyclopentane occur likewise in liquid and solid modifications. The liquid forms of these hydrocarbons are the less stable and hence change into stable solid stereoisomers upon aging.[1]

1,2-Diphenyl-tetra-cyclohexylethane, dissolved in xylene and heated to 100° for 10 minutes, formed an isomer (m.p. 209°).[474] The structure of this isomer product was considered to be related to that of *p*-benzohydryl-tetraphenylmethane (the product of isomerization of hexaphenylethane). (*p*-[Di-cyclohexylmethyl] - phenyl) (phenyl) (di - cyclohexyl) - methane and, less likely, (*m*-[phenylcyclohexylmethyl]-cyclohexyl) (phenyl) (di-cyclohexyl) methane are, therefore, hydrocarbons that may comprise the product from 1,2-diphenyl-tetra-cyclohexylethane. The first possible derivative involves the combination of an ordinary trisubstituted methyl free radical with one of its specific aryl-resonance forms; the second or less likely derivative requires the addition of the same trisubstituted methyl free radical to a hypothetical, substituted cyclohexyl free radical:



Treatment of 1,2-diphenyl-tetra-cyclohexylethane (dissolved in ether) with 40-per cent sodium amalgam, followed by carbon dioxide, gave 15 per cent of an isomer (m.p. 209°) and a certain amount of phenyl-di-cyclohexylacetic acid.[474]

The data on isomerizations of aromatic-cyclane hydrocarbons are given in Table 41, p. 390.

Conclusions

Aromatic-cyclane hydrocarbons isomerize to more stable structures upon aging, thermal treatment, or catalytic influence. Catalysts other than sulfuric acid or sodium amalgam to accelerate these interesting isomerizations remain to be found.

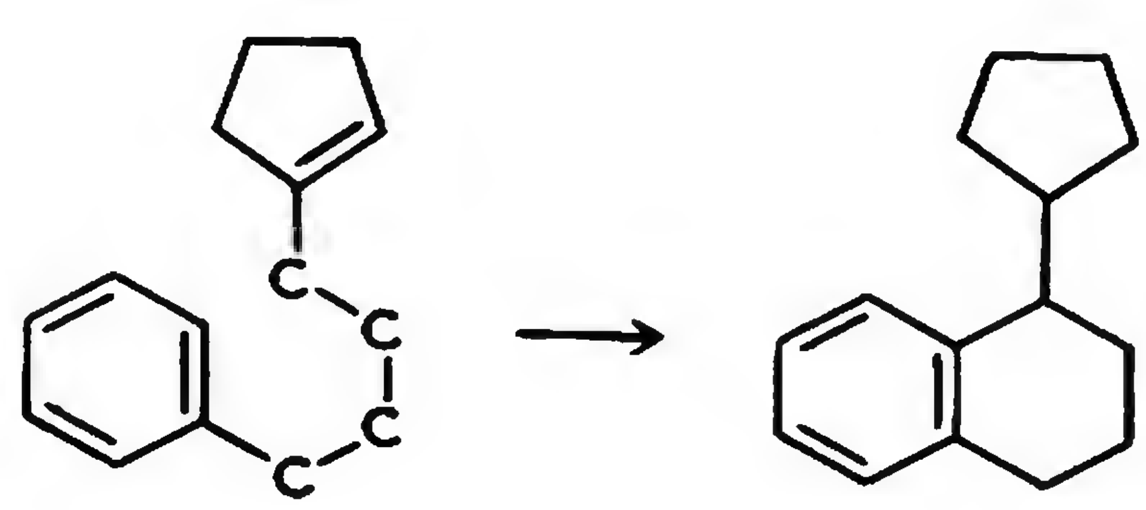
Aromatic-Cyclene Hydrocarbons

Cyclization of an aromatic-cyclene hydrocarbon occurs readily when the cyclene ring is attached univalently to the aromatic. In this reaction the ring closure upon the active double bond can be considered as an intramolecular alkylation with migration of hydrogen. The ease with which cyclization occurs in different directions makes it imperative that experimenters prove the structures and purity of both the unsaturated (reactive) and cyclized hydrocarbons concerned in these isomerizations. Some principles of ring closure governing these cyclizations have been considered in the literature.[160] Generally, the structures of only a few members command the attention of an experimenter. Vast researches are being conducted on carcinogenic and related hydrocarbons, a program which tends to revise their names and some structures.

Isomerizations

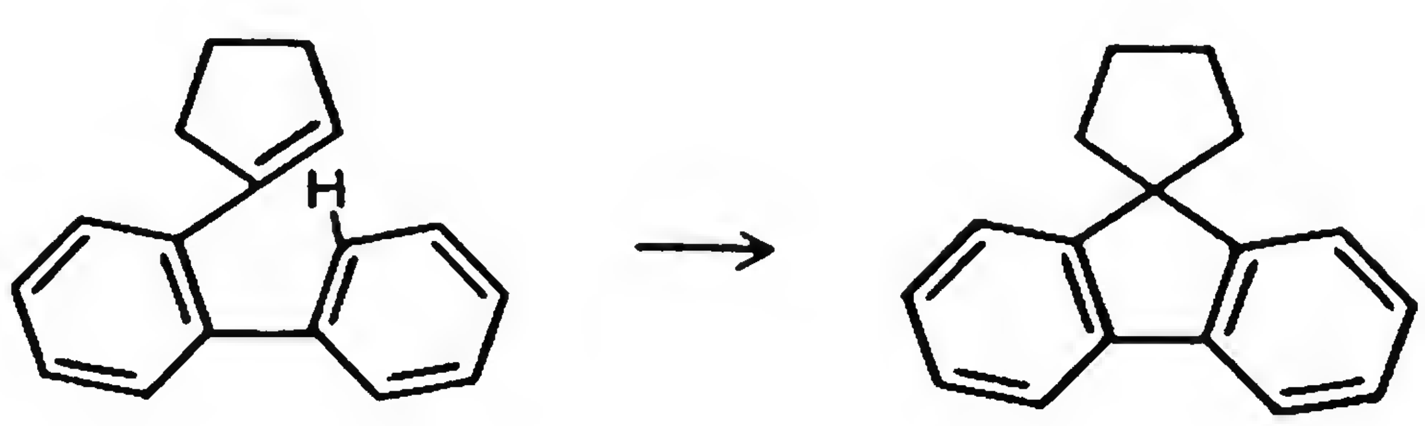
The following 37 related cyclizations are given in order of increasing size of the cyclene rings and side-chains.

1-(4-Phenylbutyl)cyclopentene-1, upon contact with cold sulfuric acid, formed 1-cyclopentyl-1,2,3,4-tetrahydronaphthalene:[134a]



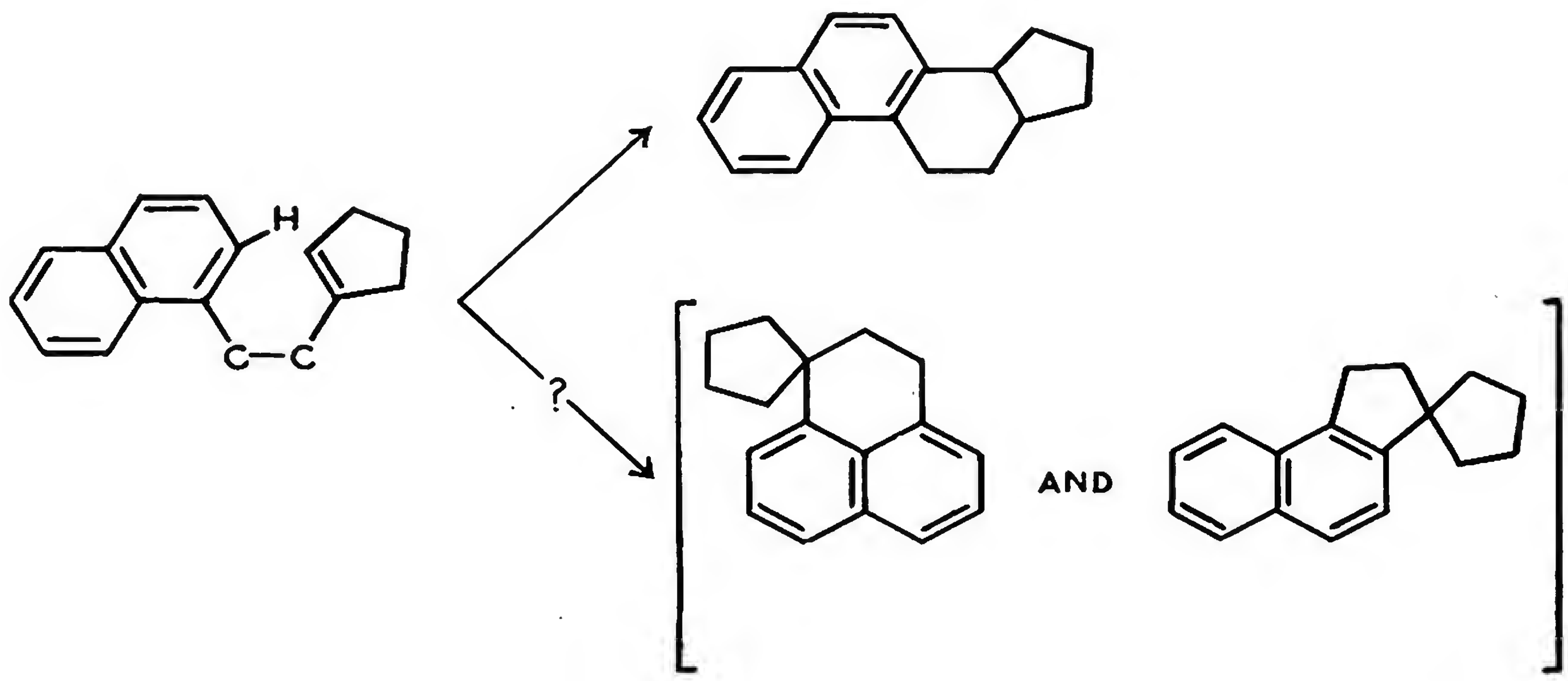
This example apparently involves an internal dehydrogenation-hydrogenation, which is a reaction effected characteristically by cold sulfuric acid.

The cyclization of 1-(*o*-biphenylyl)cyclopentene-1 (in carbon disulfide) with aluminum chloride for 5 hours at 0° resulted in the formation of 9-fluorylspirocyclopentane:[26]

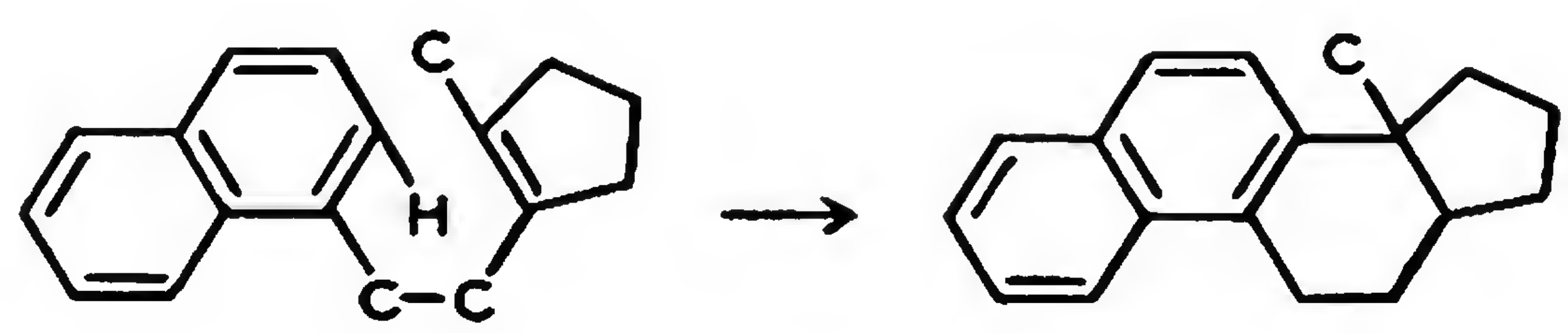


Treatment of 1-(β-1′-naphthylethyl)cyclopentene-1 (in carbon disulfide) for 24 hours at 0° with aluminum chloride gave presumably 83 per cent of *cis*- and *trans*-2,3,3a,10,11,11a-hexahydro-1-cyclopenta[a]phenanthrene (*i.e.*, 1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene).[116] Subsequent investigation [117] has indicated that the product may contain also

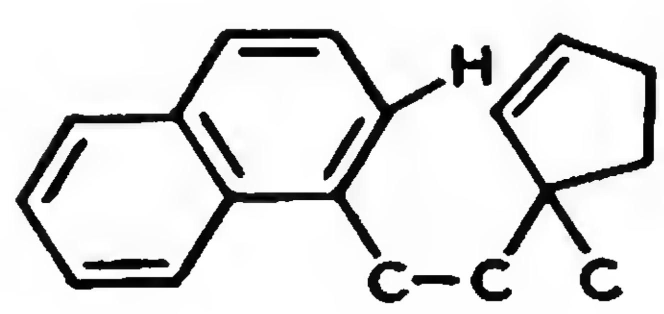
the two spiranes: 2,3-dihydro-spiro[benzonaphthene-1,1'-cyclopentane], *i.e.*, 7,8-dihydrophenalyl-7-spirocyclopentane, and 1,2-dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane]:



A carbon disulfide solution of 1-methyl-2-(β-1' naphthylethyl)cyclopentene-1 was treated overnight with aluminum chloride at 0°, giving 50 per cent of 3a-methyl-2,3,3a,10,11,11a-hexahydro-1-cyclopenta[a]-phenanthrene, *i.e.*, 1-methyl-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene:[321]

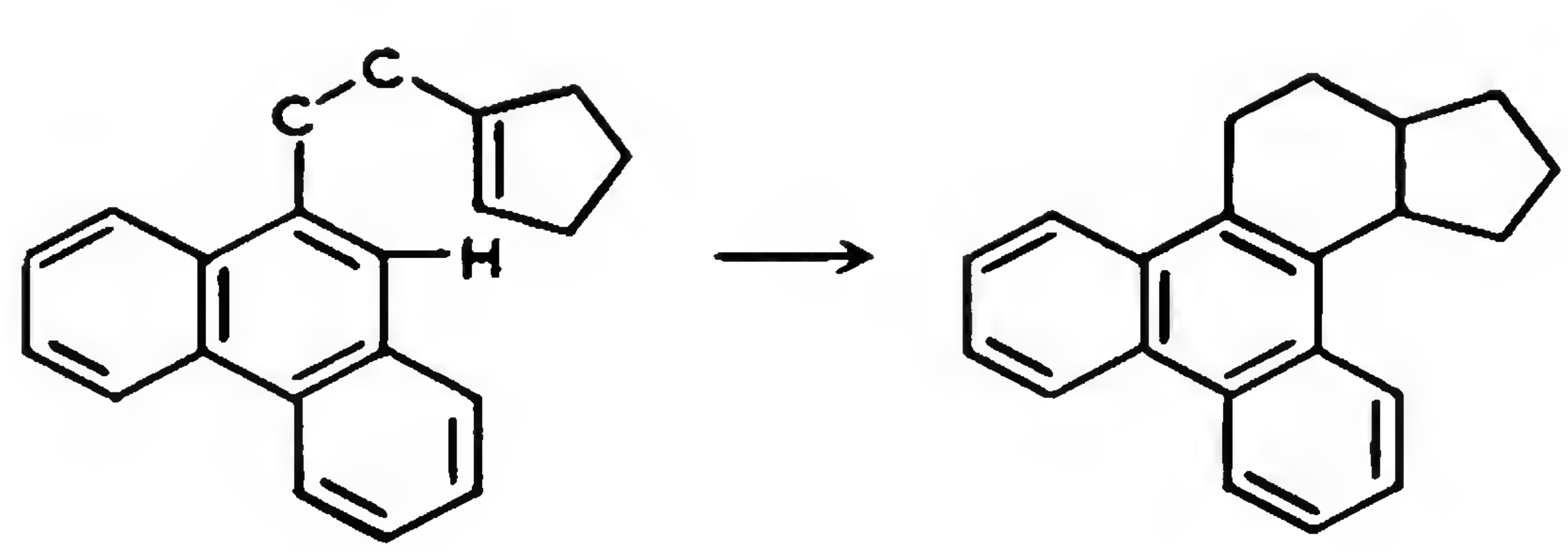


The related 1-methyl-1-(β-1'-naphthylethyl)cyclopentene-2, however, could not be cyclized by any of the reagents tried, including aluminum chloride.[321]

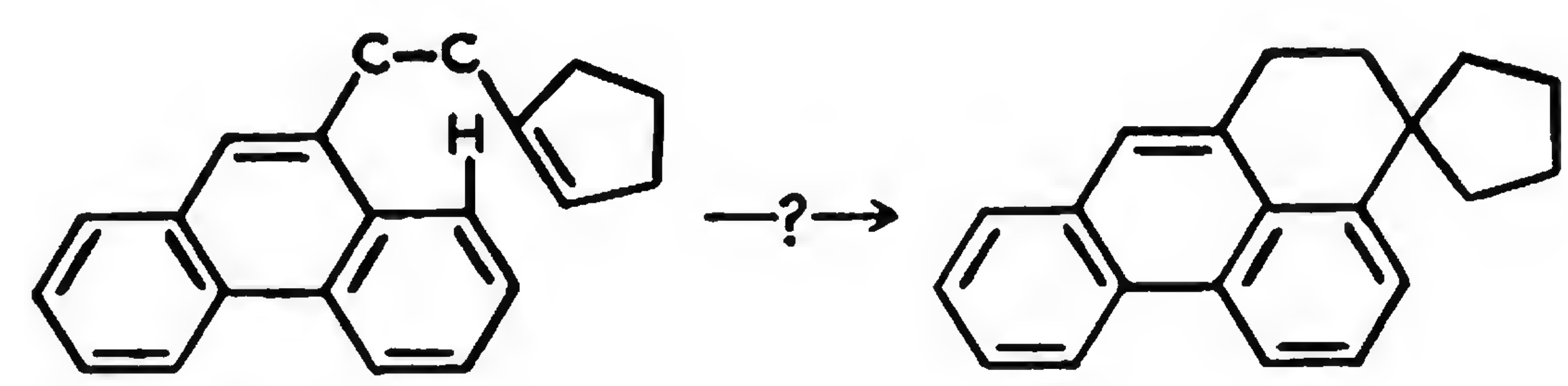


[Unisomerized to date]

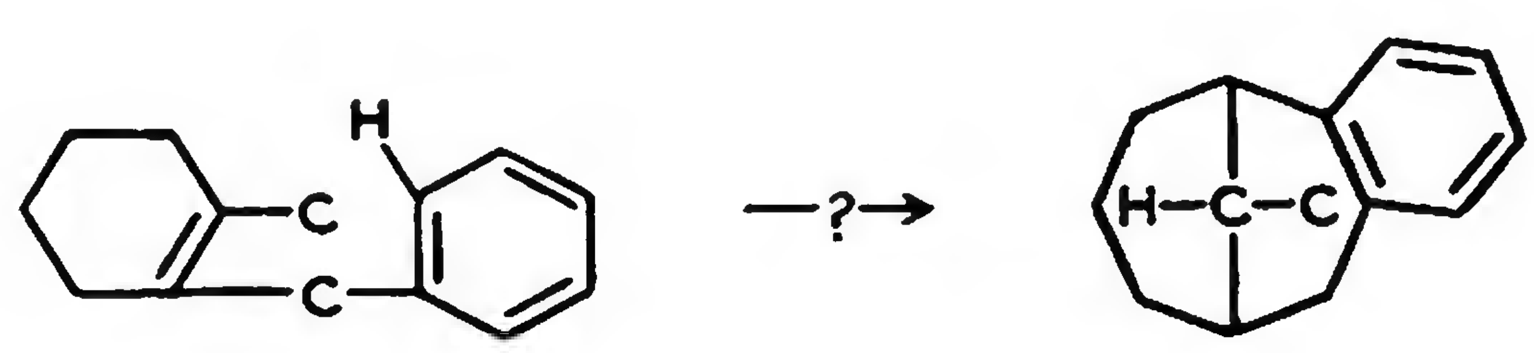
1-(β-9'-Phenanthrylethyl)cyclopentene-1, treated in carbon disulfide solution at room temperature for 12 hours with aluminum chloride, gave 49 per cent of tetrahydrocyclopentenotriphenylene:[49]



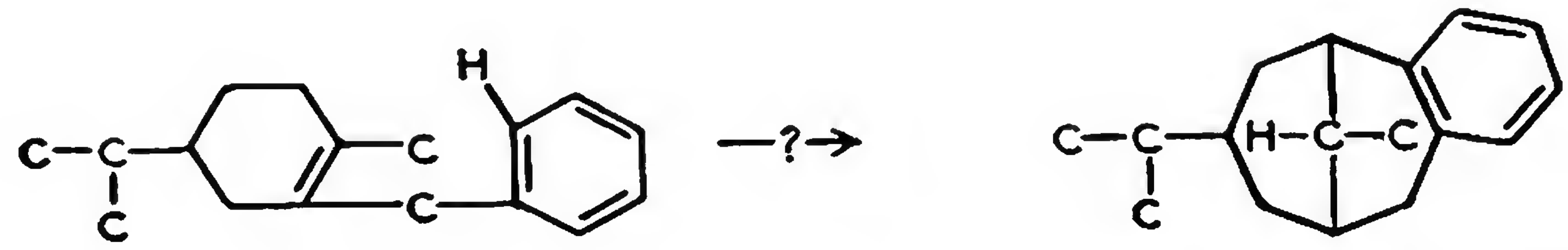
Since subsequent dehydrogenation is alleged to produce a methyl-3,4-benzpyrene, the reaction has been interpreted as giving instead the dihydro-6-meso-benzanthrenespirocyclopentane.[250] Another investigation [48] makes the structure of the isomer product even more uncertain.



The cyclizations of 1-methyl-2-benzylcyclohexene-1 for 3 hours, and of 1-methyl-2-benzyl-4-isopropylcyclohexene-1 for 5 hours, both with aluminum chloride at 0°, gave isomers without an active double bond.[118] It was shown that the cyclization products (70 and 75 per cent, respectively) cannot be hexahydrofluorenes, although it was not proved that there is a formation of the alternative benzbicyclononenes. Assuming the formation of the last hydrocarbons, the reactions can be given as follows:



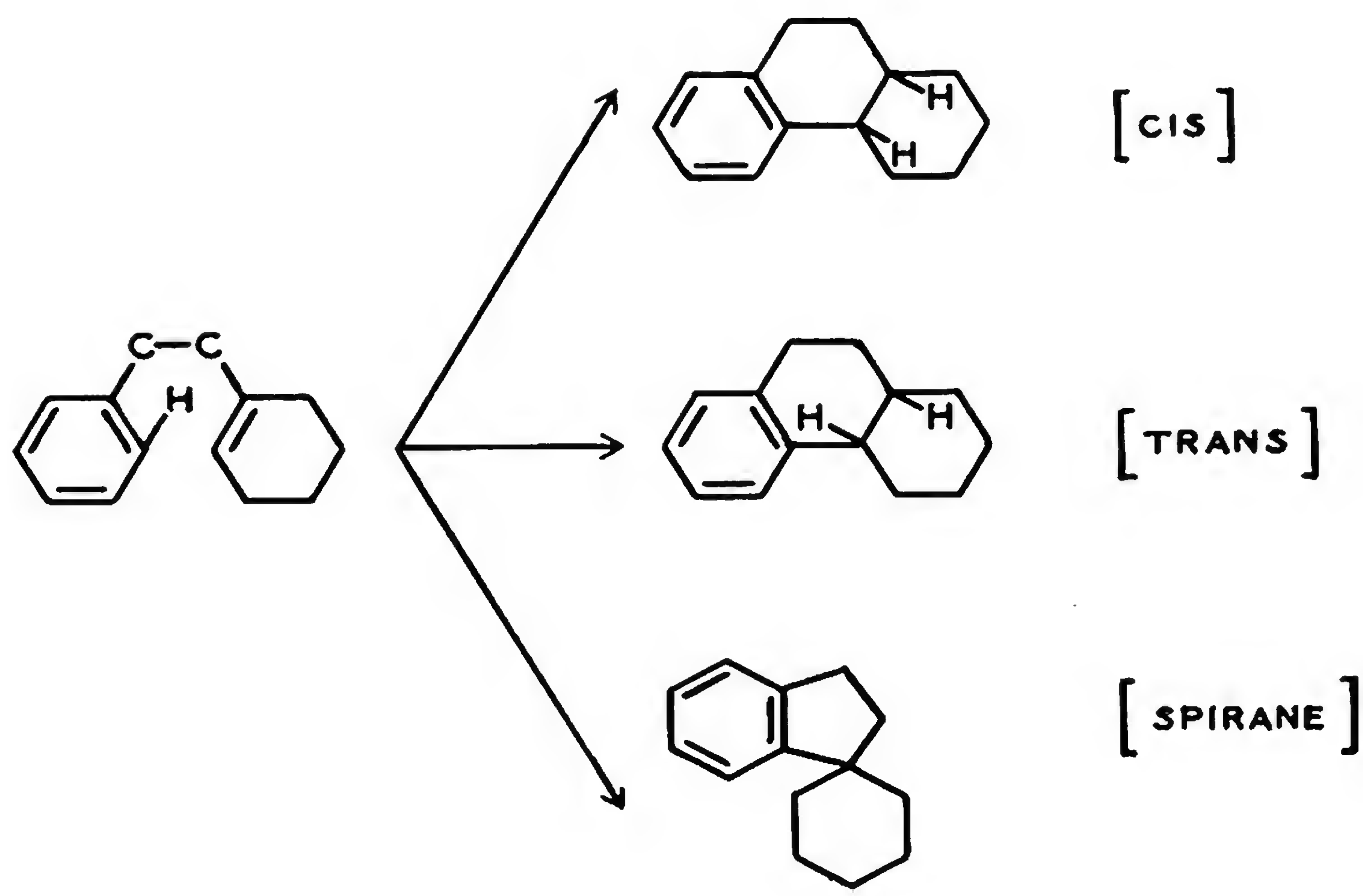
2-Methyl-2,3-benzbicyclo-[3.3.1]nonene-2



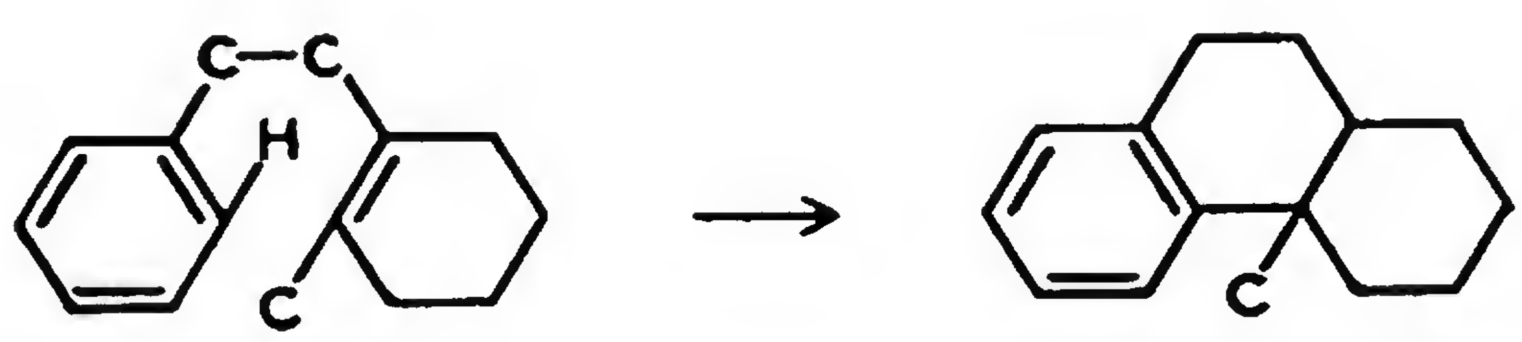
7-Isopropyl-9-methyl-2,3-benzbicyclo[3.3.1]nonene-2

Apparently, the strainless bicyclononene system is formed in preference to the hexahydrofluorenes, but even this requires an initial isomerization into cyclohexene-5 (or -6) hydrocarbons.

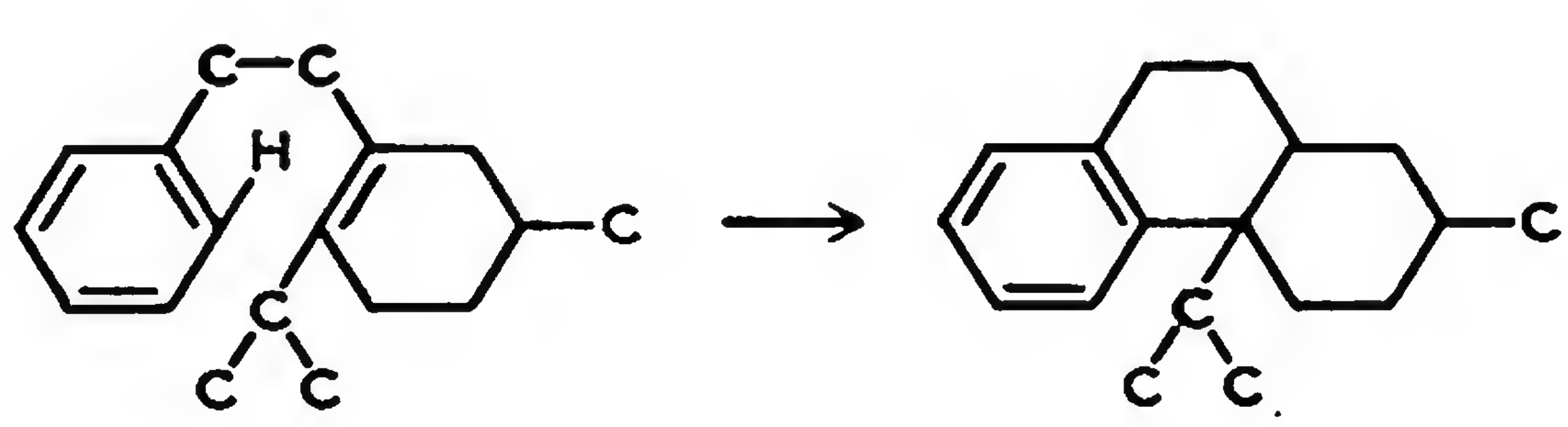
Isomerization of 1-(β-phenethyl)cyclohexene-1, in carbon disulfide solution with aluminum chloride for 6 hours,[114] or for 24 hours,[116] gave 1,2,3,4,4a,9,10,10a-octahydrophenanthrene. The yield in the 24-hour treatment was 49 per cent. Later work on the cyclization with aluminum chloride indicated that, depending on reaction conditions (undisclosed), the product consists of much *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene, less of the *trans* form, and a still smaller amount of hydrindene-spirocyclohexane.[120] 1-(β-Phenethyl)cyclohexene-1 gave 1,2,3,4,4a,9,10,-10a-octahydrophenanthrene when treated with concentrated sulfuric acid [434] or with acetic acid plus sulfuric acid:[116]



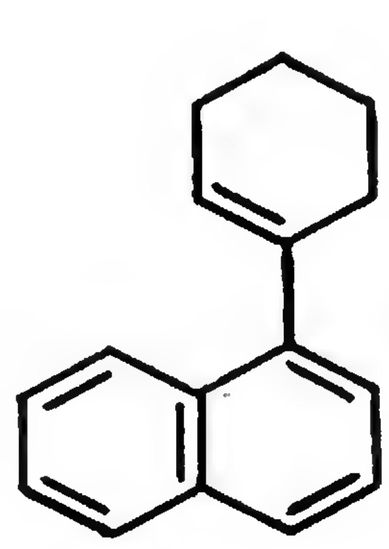
The isomerization of 1-methyl-2-(β-phenethyl)cyclohexene-1 with aluminum chloride plus carbon disulfide at 0° gave 70 per cent of 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (*i.e.*, 12-methyl-1,-2,3,4,9,10,11,12-octahydrophenanthrene:[321]



The cyclization of 1-isopropyl-2-(β-phenethyl)-4-methylcyclohexene-1 into 2-methyl-4a-isopropyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (*i.e.*, 2-methyl-12-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene) occurred almost quantitatively in the presence of concentrated sulfuric acid, but not at all with 90-per cent sulfuric acid in the cold:[427]

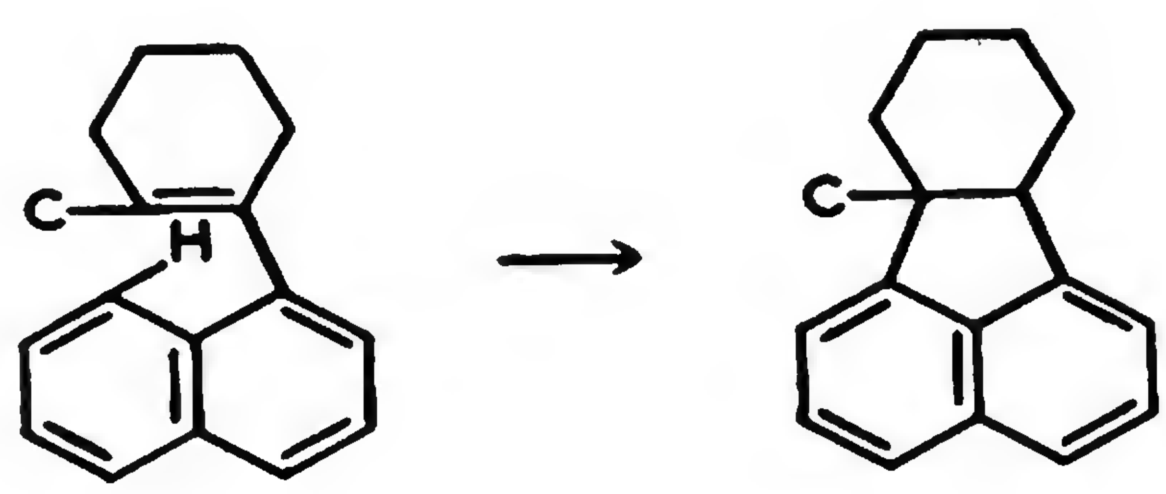


An attempt at the cyclization of 1-(1′-naphthyl)cyclohexene-1 was unsuccessful.[121]

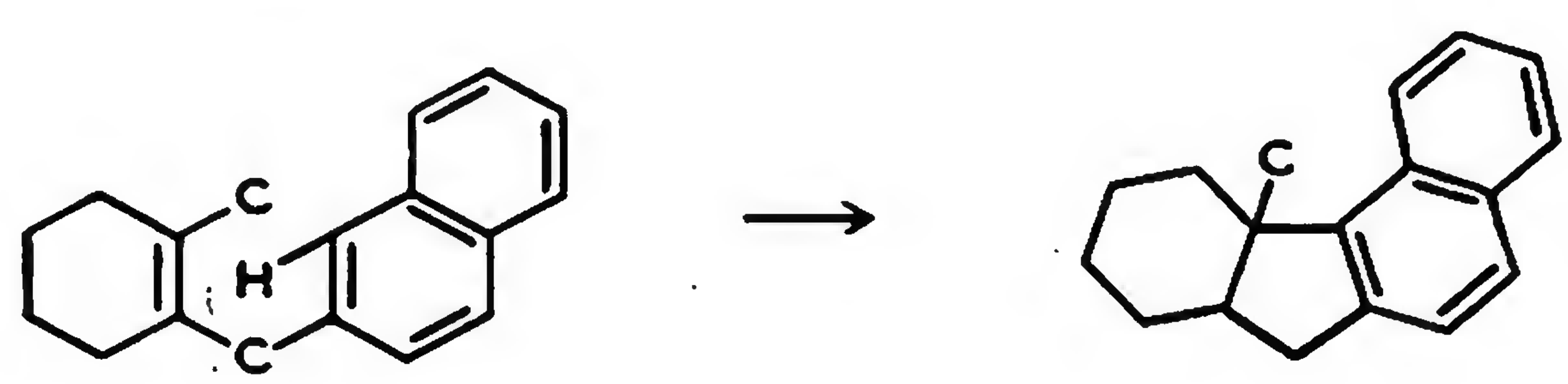


[Unisomerized to date]

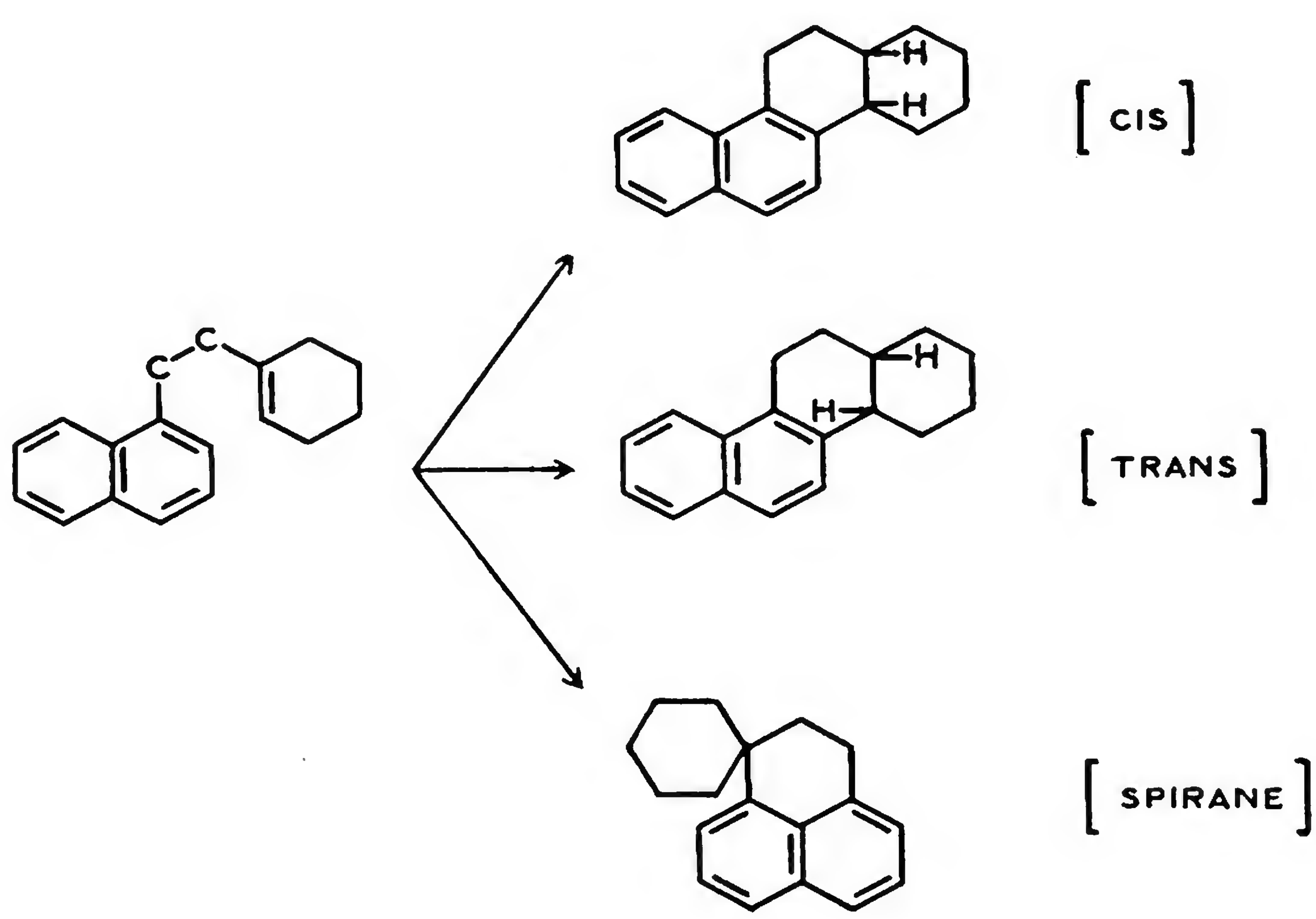
1-Methyl-2-(1′-naphthyl)cyclohexene-1 when treated with aluminum chloride plus carbon disulfide at 0° was cyclized to 6b-methyl-6b,7,8,9,-10,10a-hexahydrofluoranthene:[121]



Treatment of 1-methyl-2-(2′-naphthylmethyl)cyclohexene-1, in carbon disulfide solution for 6 hours at 0° with aluminum chloride, gave 47 per cent of 11a-methyl-7a,8,9,10,11,11a-hexahydro-7-benzo[c]fluorene, *i.e.*, 7a,8,9,10,11,11a-hexahydro-11a-methyl-3,4-benzofluorene:[113]

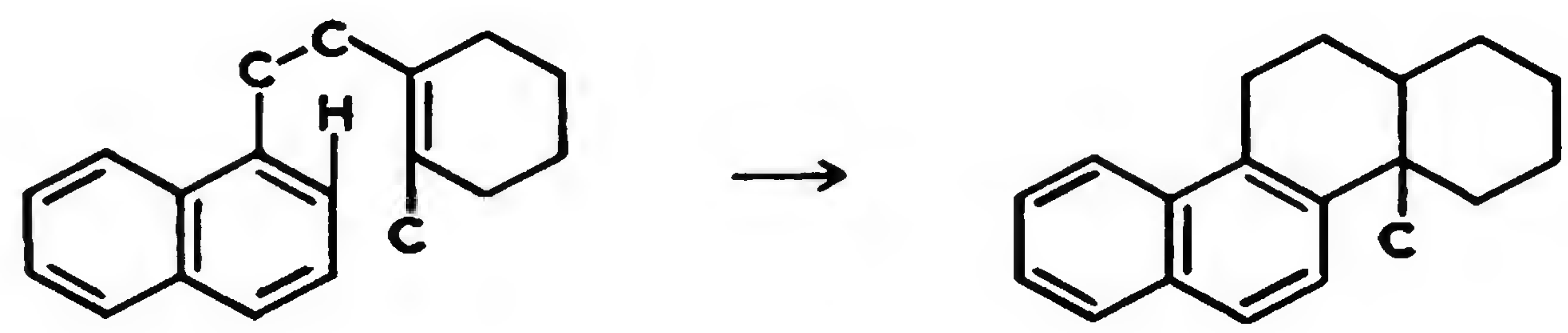


The action of aluminum chloride upon 1-(β-1′-naphthylethyl)-cyclohexene-1 in carbon disulfide at 0° led to a mixture of *cis*- and *trans*-1,-2,3,4,4a,11,12,12a-octahydrochrysenes and 2,3-dihydro-spiro[benzonaphthene-1,1′-cyclohexane], *i.e.*, 7,8-dihydrophenalyl-7-spirocyclohexane:[117]

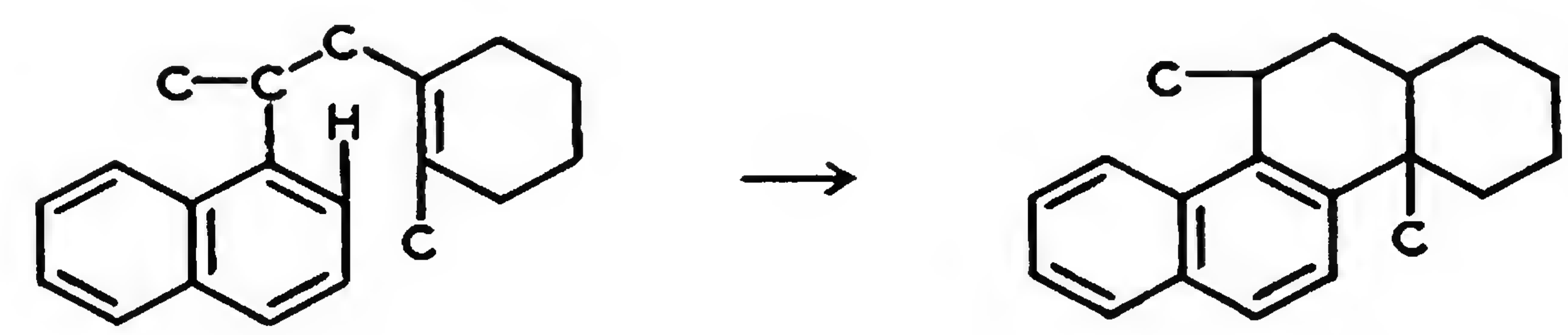


The cyclization of 1-methyl-2-(β-1′-naphthylethyl)cyclohexene-1, *i.e.*, 1-(β-[2-methylcyclohex-1-en-1-yl]ethyl)naphthalene, in carbon disulfide solution for 7 hours at 0° with aluminum chloride, gave 60 per

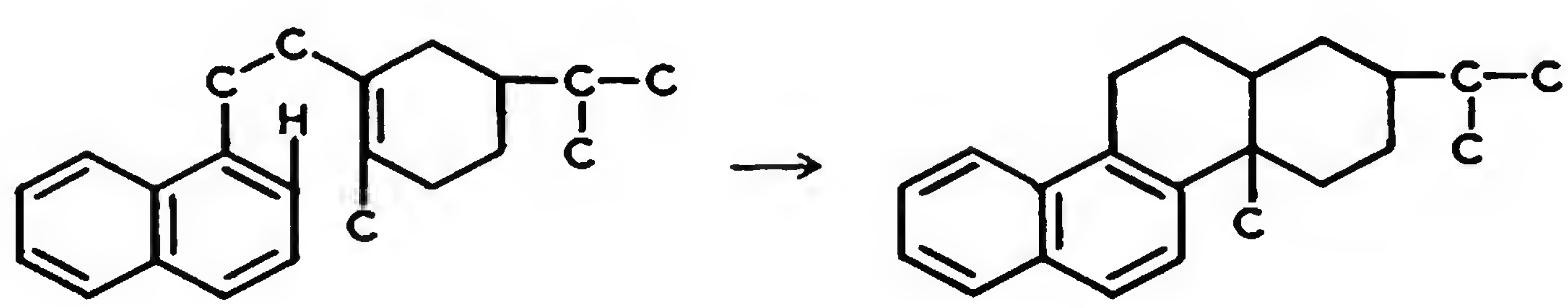
cent of 4a-methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene, formerly named 1,2,2a,3,4,5,6,6a-octahydro-6a-methylchrysene:[115]



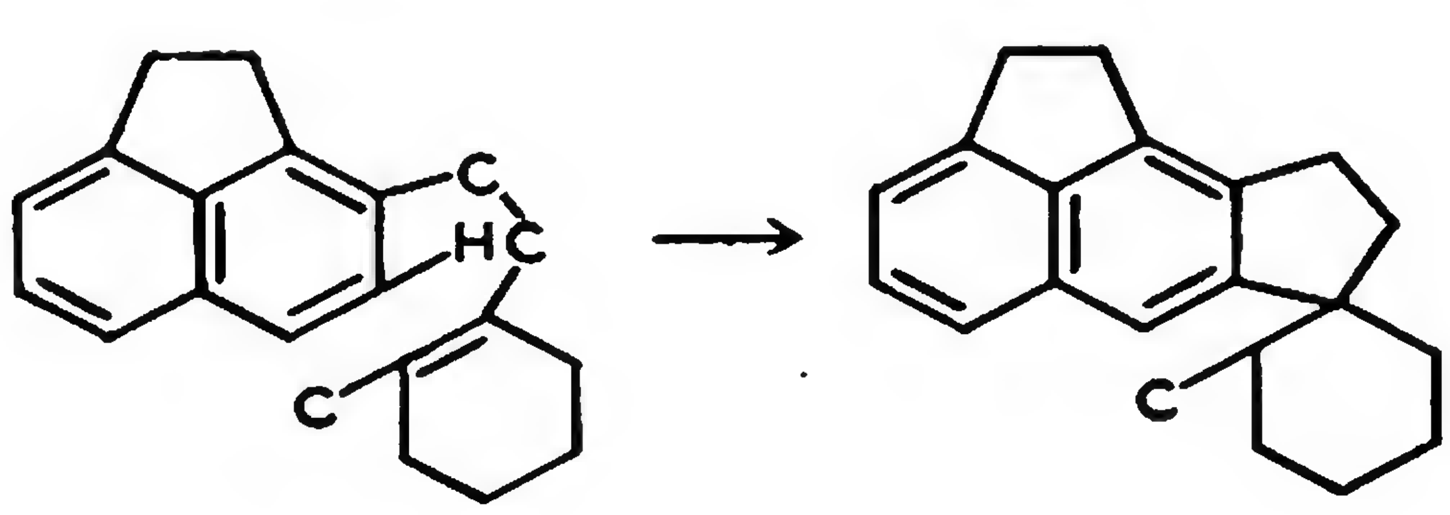
The reaction of 1-methyl-2-(β-1′-naphthyl-*n*-propyl)cyclohexene-1, *i.e.*, 1-(2-methylcyclohex-1-en-1-yl)-2-(α-naphthyl)propane or 1-(β-[2-methylcyclohex-1-en-1-yl]isopropyl)naphthalene, with aluminum chloride plus carbon disulfide for 21 hours at 0°, yielded 72 per cent of 4a,11-dimethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene ("5,10a-dimethyl - as-octahydrochrysene"): [186]



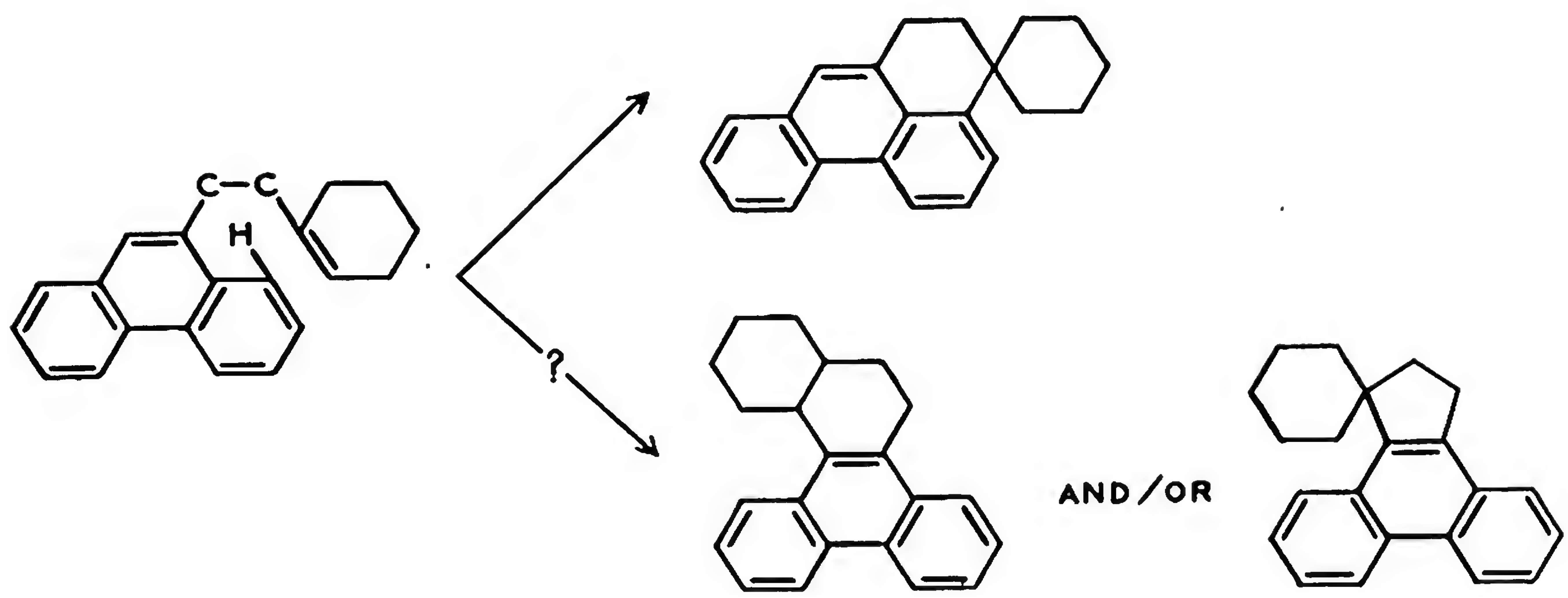
Cyclization of 1-methyl-2-(β-1′-naphthylethyl)-4-isopropylcyclohexene-1, *i.e.*, 1-(β-[1-methyl-4-isopropylcyclohex-1-en-2-yl]ethyl)-naphthalene, with aluminum chloride plus carbon disulfide for 24 hours at 0°, gave 2-isopropyl-4a-methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene:[123]



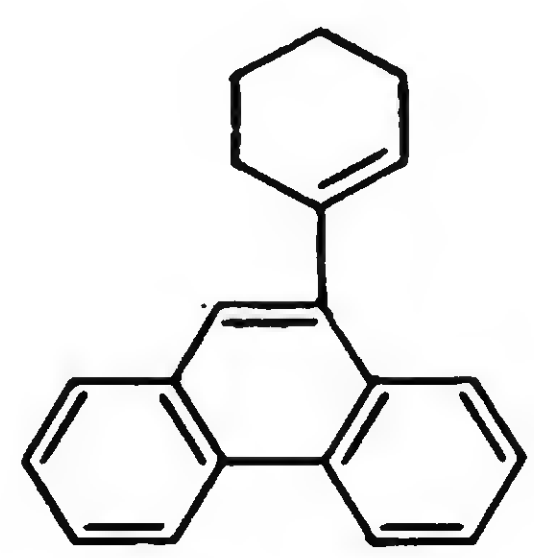
Treatment of 1-methyl-2-(β-3′-acenaphthylethyl)cyclohexene-1, *i.e.*, 3-(β-[2-methylcyclohex-1-en-1-yl]ethyl)acenaphthene, with aluminum chloride plus carbon disulfide (for 21 hours at 0°) gave 8,9-dihydro-2′-methyl-spiro[β-acenaphthindan-3,1′-cyclohexane]: [115]



An attempted cyclization of 1-(β-9′-phenanthrylethyl)cyclohexene-1 into octahydro-1,2,3,4-dibenzphenanthrene, by aluminum chloride plus carbon disulfide at 0°, gave a spirane, probably a dihydrobenzanthrene-spirocyclohexane.[250] The formation of dihydrocyclopenta[*l*]phenanthrenespirocyclohexane, however, was not excluded:

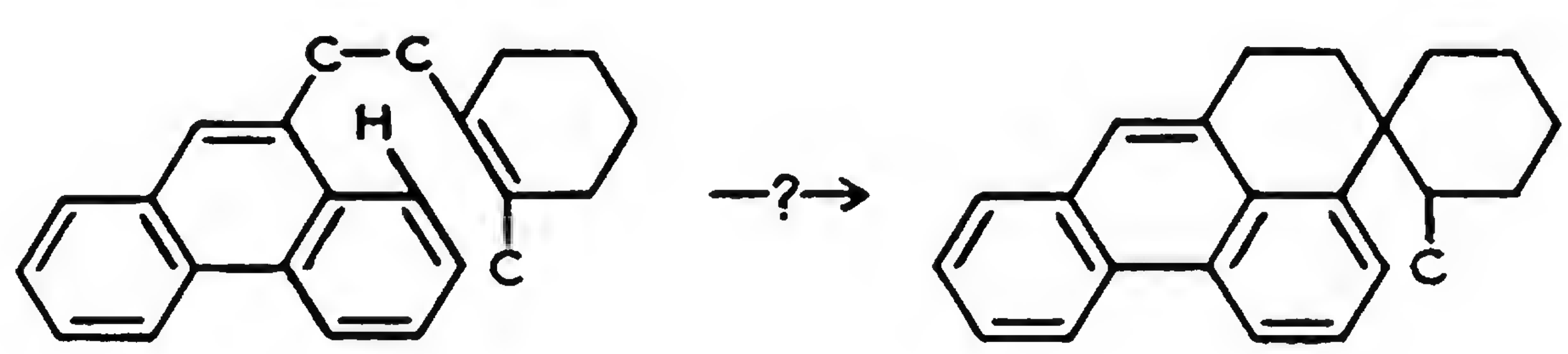


Cyclization of 9-cyclohexenylphenanthrene into 5,6-benzofluoranthene by treatment with carbon disulfide and aluminum chloride for 24 hours at 0° was a failure.[47]

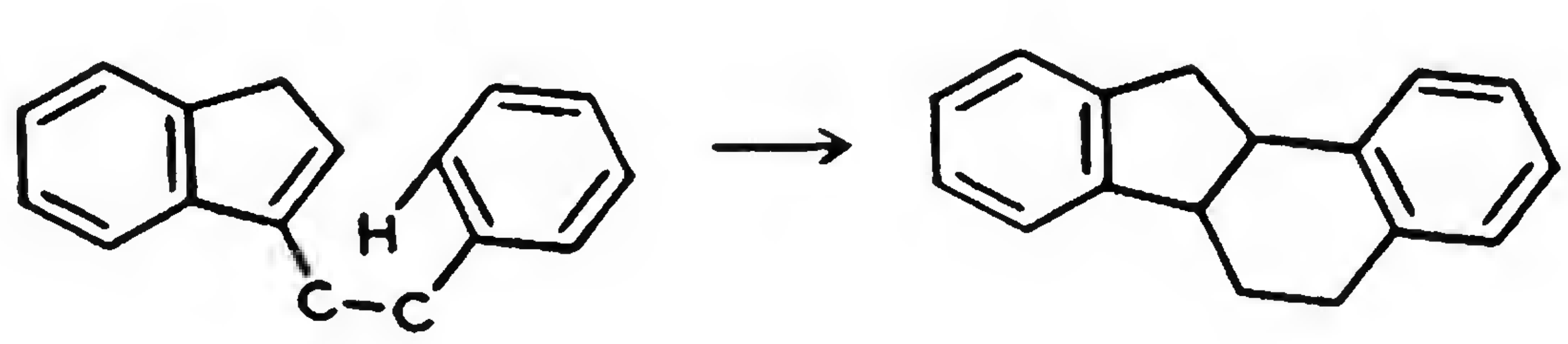


[Unisomerized to date]

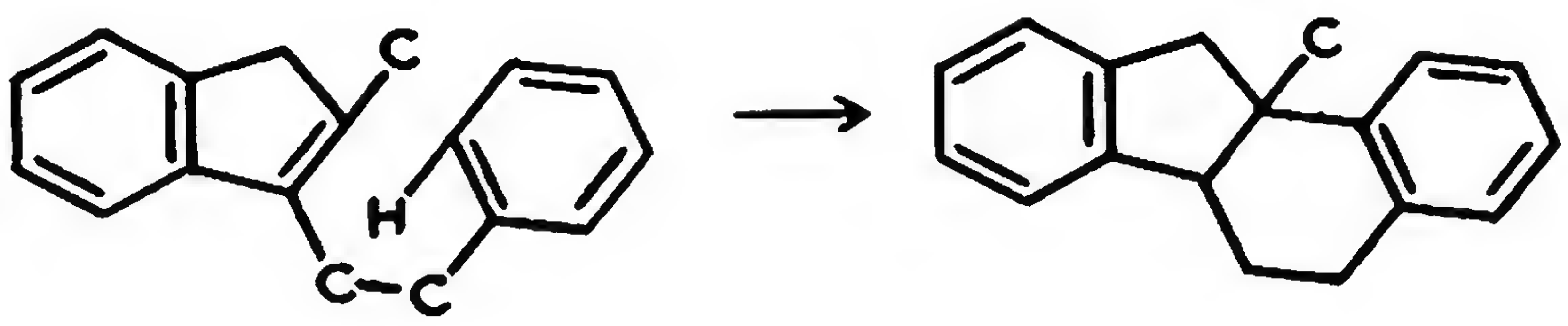
Isomerization of 1-methyl-2-(β-9′-phenanthrylethyl)cyclohexene-1 with aluminum chloride did not always give satisfactory results, but treatment with hydrogen chloride plus stannic chloride gave 80 per cent of a presumable spirane.[45] The structure of the last product may be that of a dihydrobenzanthrenespiromethylcyclohexane.



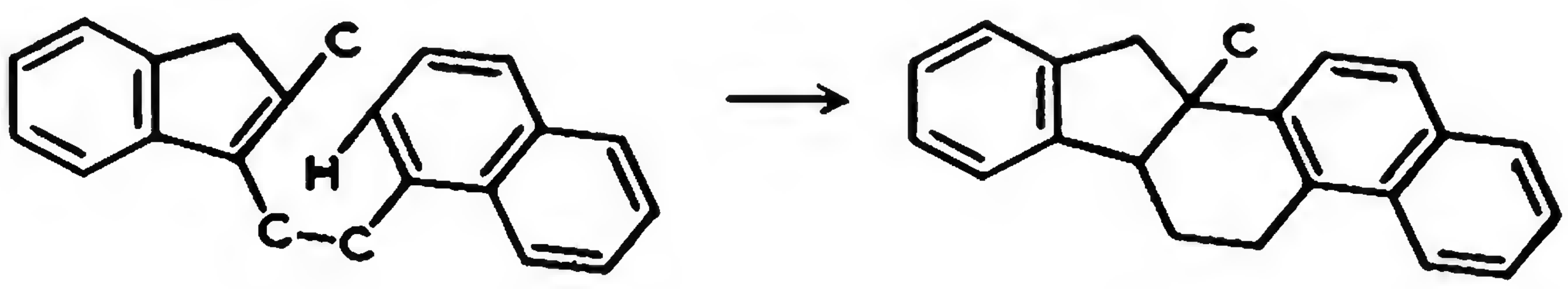
The reaction of 3-(β-phenethyl)indene with aluminum chloride and carbon disulfide at 0°, or with acetic acid containing sulfuric acid at 100°, resulted respectively in 18 and 16 per cent of 5,6,6a,11a-tetrahydrochrysofluorene:[117]



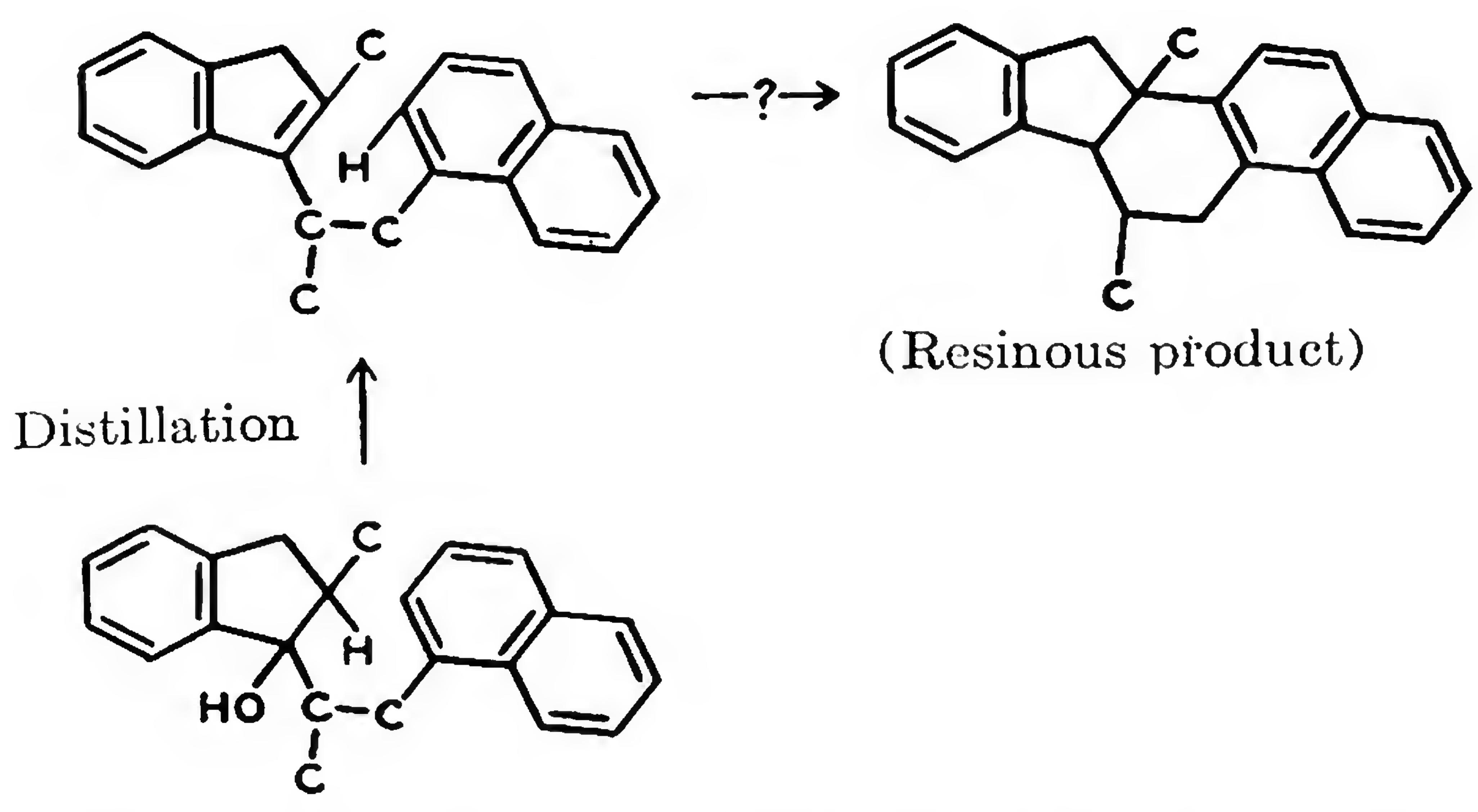
Treatment of 2-methyl-3-(β-phenethyl)indene (in carbon disulfide solution with aluminum chloride for 3 hours at 0°) yielded 82 per cent of 5,6,6a,11a-tetrahydro-11a-methylchrysofluorene:[119]



The cyclization of 2-methyl-3-(β-1′-naphthylethyl)indene with aluminum chloride and carbon disulfide (for 3 hours at 0°) resulted in 77.1 per cent of crude and 27.2 per cent of pure 11a-methyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene, *i.e.*, 10-methyl-3,4,10,11-tetrahydro-2′,1′-naphtha-1,2-fluorene:[25]

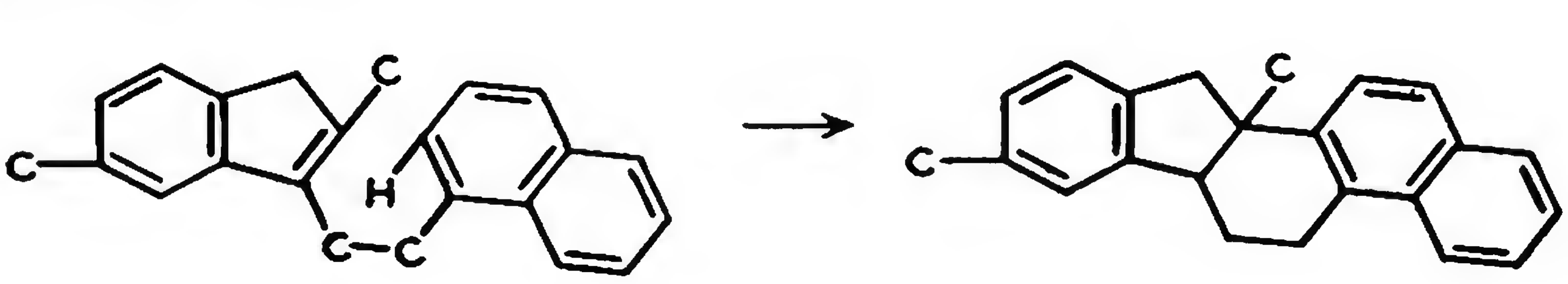


The formation of a resinous liquor by the treatment of a distillation product from 1-(β-1′-naphthylisopropyl)-2-methyl-indanol-1, with aluminum chloride plus carbon disulfide at 2-3° C., can be taken as the formation of 6,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 4,10-dimethyl-3,4,10,11-tetrahydro-2′,1′-naphtha-1,2-fluorene) from 2-methyl-3-(β-1′-naphthylisopropyl)indene [*i.e.*, 1-(α-naphthyl)-2-(2-methylindenyl-3)-propane or 1-(β-[2-methylindenyl-3]propyl)-naphthalene]:[25]

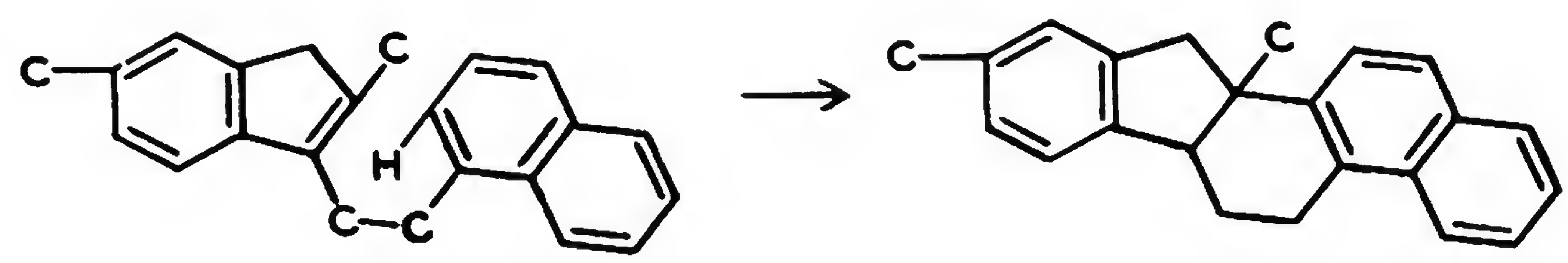


A selenium dehydrogenation was conducted upon the resinous product; its results confirm the foregoing interpretation of the cyclization.

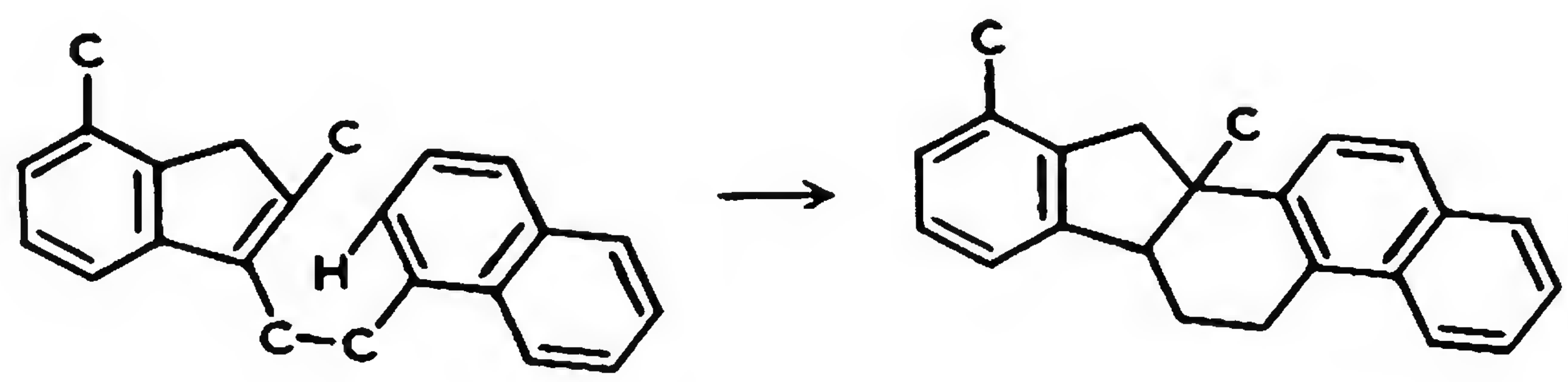
The treatment of 2,5-dimethyl-3-(β-1′-naphthylethyl)indene with aluminum chloride plus carbon disulfide for 3 hours at 0° gave 75.5 per cent of crude and 18.9 per cent of pure 8,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 6,10-dimethyl-3,4,10,11-tetrahydro-2′,1′-naphtha-1,2-fluorene):[25]



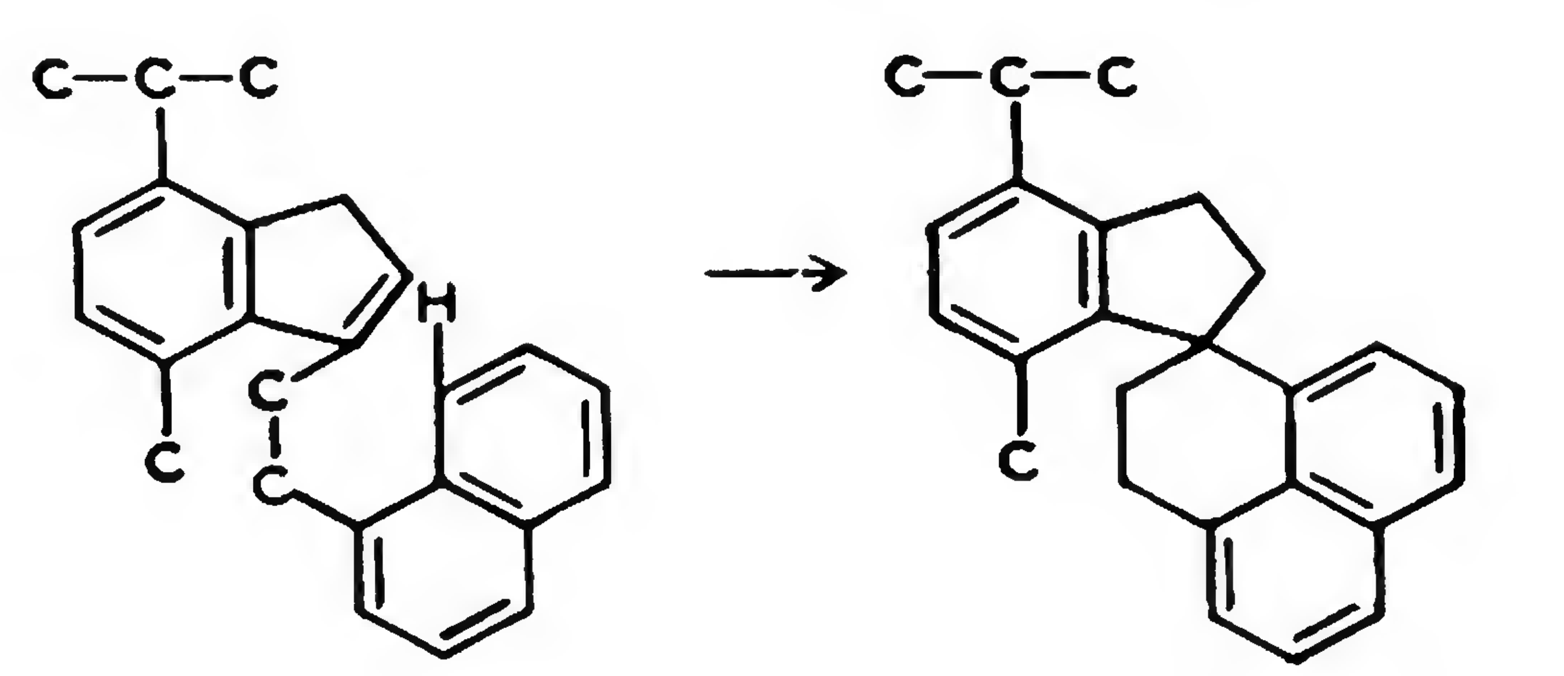
The isomerization of an impure (88.9 per cent pure ?) 2,6-dimethyl-3-(β-1′-naphthylethyl)indene with aluminum chloride plus carbon disulfide for 3 hours at 0° gave 67.5 per cent of crude (corrected for known impurity) and 5.0 per cent of pure 9,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 7,10-dimethyl-3,4,10,11-tetrahydro-2′,1′-naphtha-1,2-fluorene):[25]



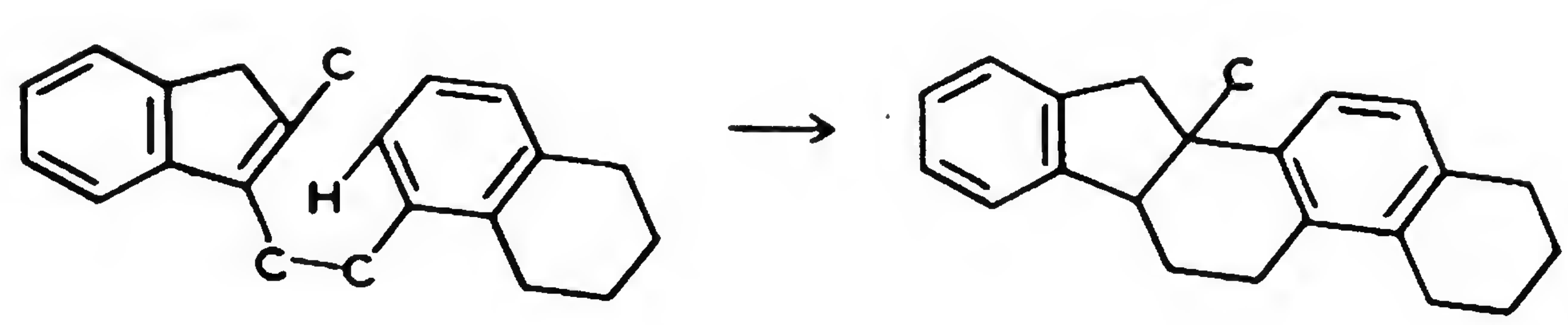
The reaction of 2,7-dimethyl-3-(β-1′-naphthylethyl)indene with aluminum chloride plus carbon disulfide, for 3 hours at 0°, resulted in the formation of 80.9 per cent of crude and 19.1 per cent of pure 10,11a-dimethyl-5,6,6a,11a-tetrahydro-11-naphtho[2,1-a]fluorene (*i.e.*, 8,10-dimethyl-3,4,10,11-tetrahydro-2′,1′-naphtha-1,2-fluorene):[25]



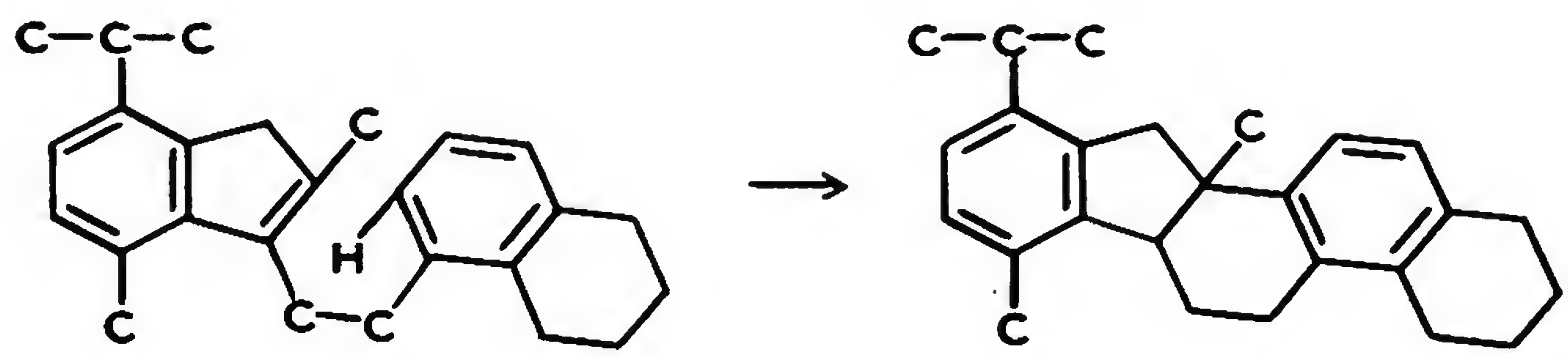
3-(β-1′-Naphthylethyl)-4-methyl-7-isopropylindene was isomerized by aluminum chloride plus carbon disulfide (within 4 hours at 0°) into 2,3-dihydro-4′-isopropyl-7′-methyl-spiro[benzonaphthene-1,1′-indan]:[119]



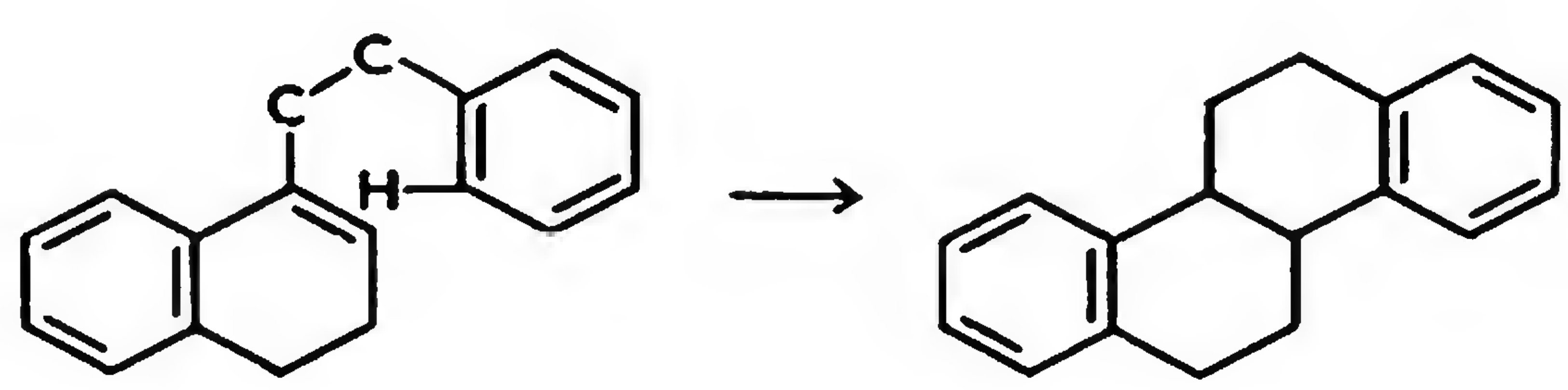
Treatment of 2-methyl-3-(β-[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)-indene [*i.e.*, 1,2,3,4-tetrahydro-5-(β-[2-methyl-3-indenyl]-ethyl)naphthalene] with aluminum chloride plus carbon disulfide for 3 hours at 0°, gave 80 per cent of 1,2,3,4,5,6,6a,11a-octahydro-11a-methyl-11-naphtho-[2,1-a]fluorene.[119] The same product resulted in a cyclization at 100° with acetic acid containing sulfuric acid:[119]



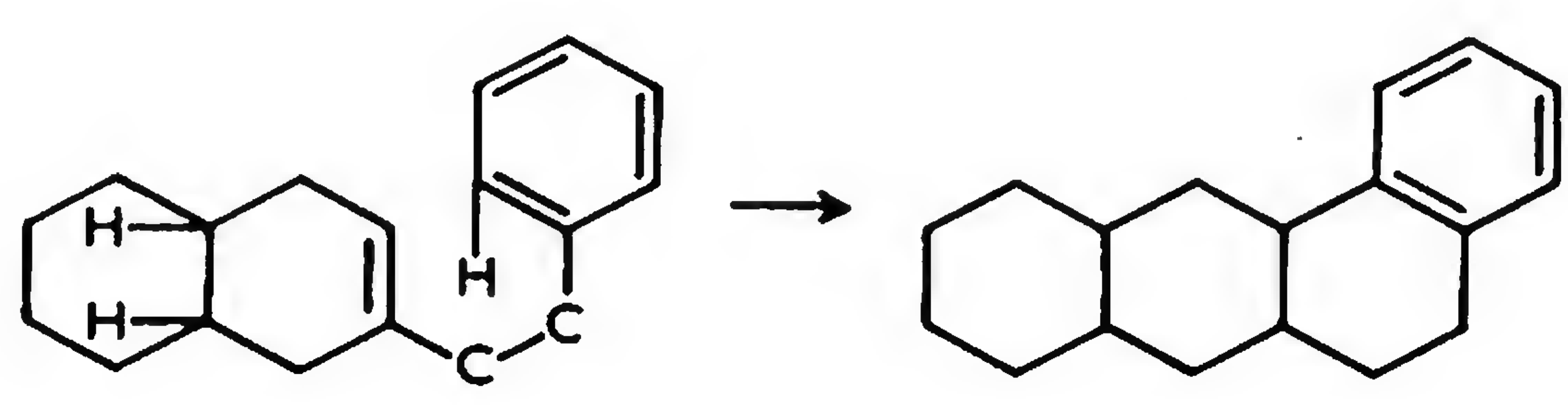
Isomerization of 2,4-dimethyl-3-(β-[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)-7-isopropylindene, *i.e.*, 1,2,3,4-tetrahydro-5-(β-[2,4-dimethyl-7-isopropyl-3-indenyl]ethyl)naphthalene, with aluminum chloride plus carbon disulfide for 3 hours at 0°, gave 75 per cent of 1,2,3,4,5,6,6a,11a-octahydro-7,11a-dimethyl-10-isopropyl-11-naphtho [2,1-a] fluorene.[119] The same product results in a cyclization at 100° with acetic acid containing sulfuric acid:[119]



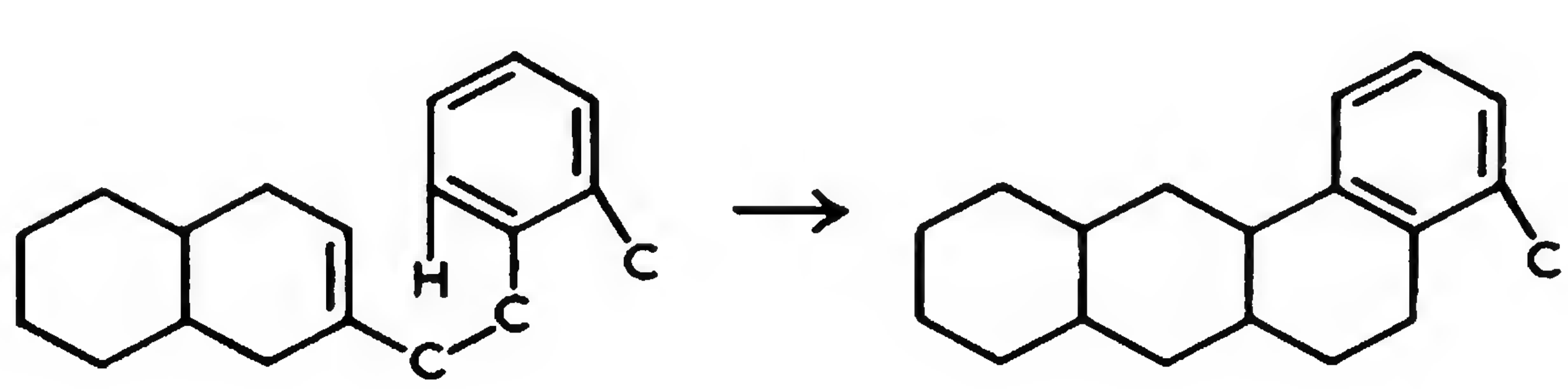
The action of aluminum chloride upon 1-(β-phenethyl)-3,4-dihydronaphthalene (in carbon disulfide at 0°) gave only 0.5 per cent of 4b,5,6,-10b,11,12-hexahydrochrysene, along with 53.2 per cent of 1-(β-phenethyl)-naphthalene as a dehydrogenation by-product:[117]



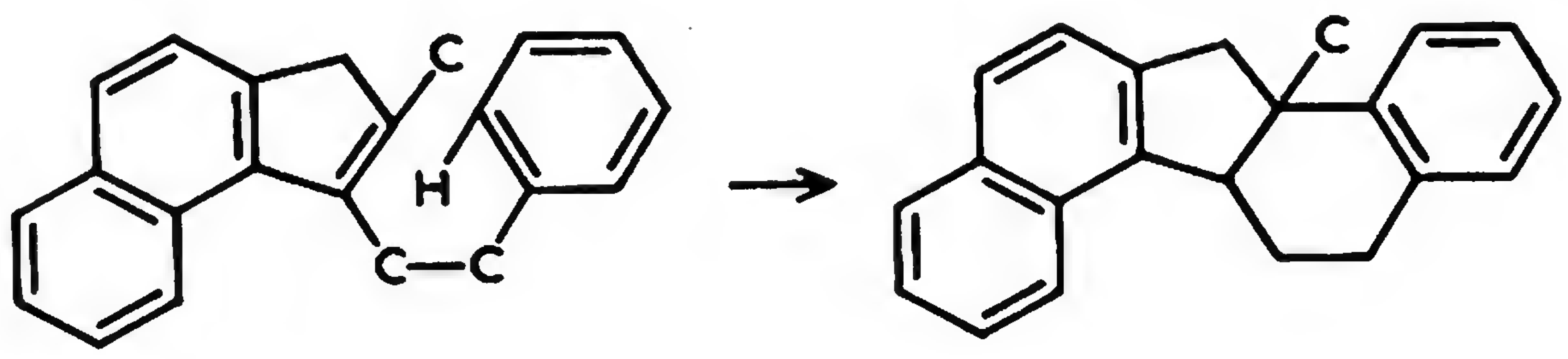
Cyclization of 2-(β-phenethyl)-*cis*-Δ^2-octalin with aluminum chloride plus carbon disulfide for 3 hours at 0°, and then for several hours at room temperature, gave some 83 per cent of dodecahydro-1,2-benzanthracene.[122] A previous experiment resulted in a total of 34.9 per cent of *cis* and *trans* isomerides of dodecahydro-1,2-benzanthracene:[117]



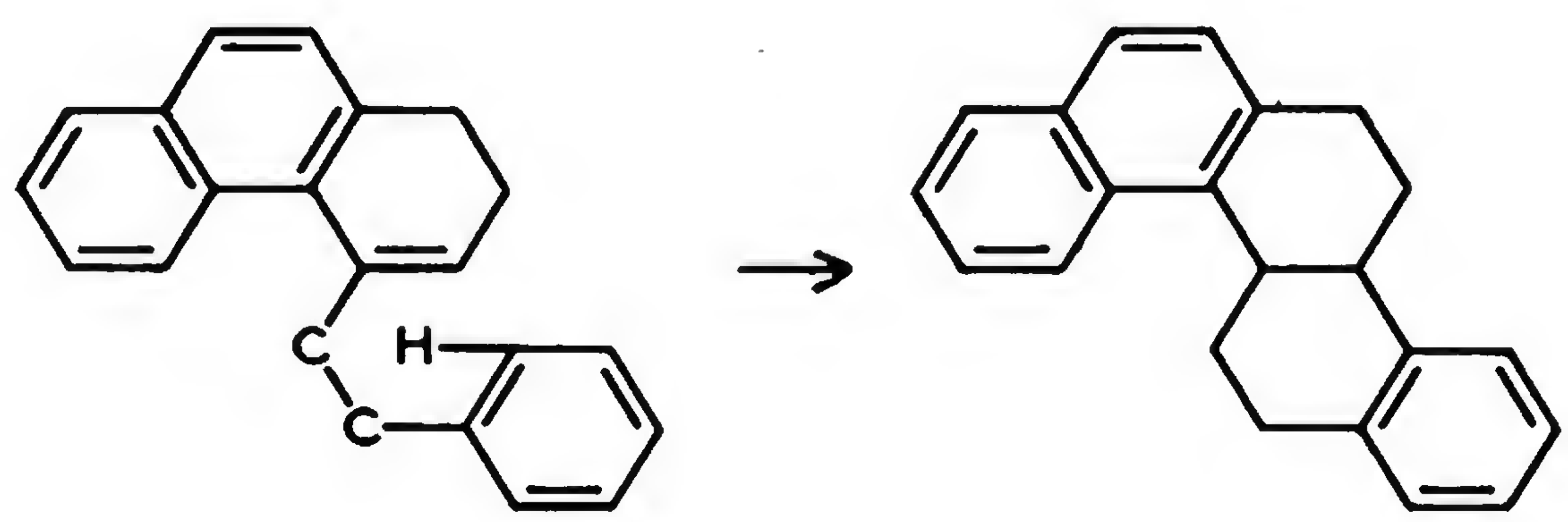
Gradual addition of aluminum chloride at 0° to a carbon disulfide solution of 2-(β-*o*-tolylethyl)-Δ^2-octalin, *i.e.*, 1,4,4a,5,6,7,8,8a-octahydro-2-(*o*-methyl-β-phenethyl)naphthalene, resulted in a 7.1 per cent formation of 4′-methyldodecahydro-1,2-benzanthracene, *i.e.*, 4-methyl-5,6,6a,-7,7a,8,9,10,11,11a,12,12a-dodecahydrobenz[a]anthrene:[124]



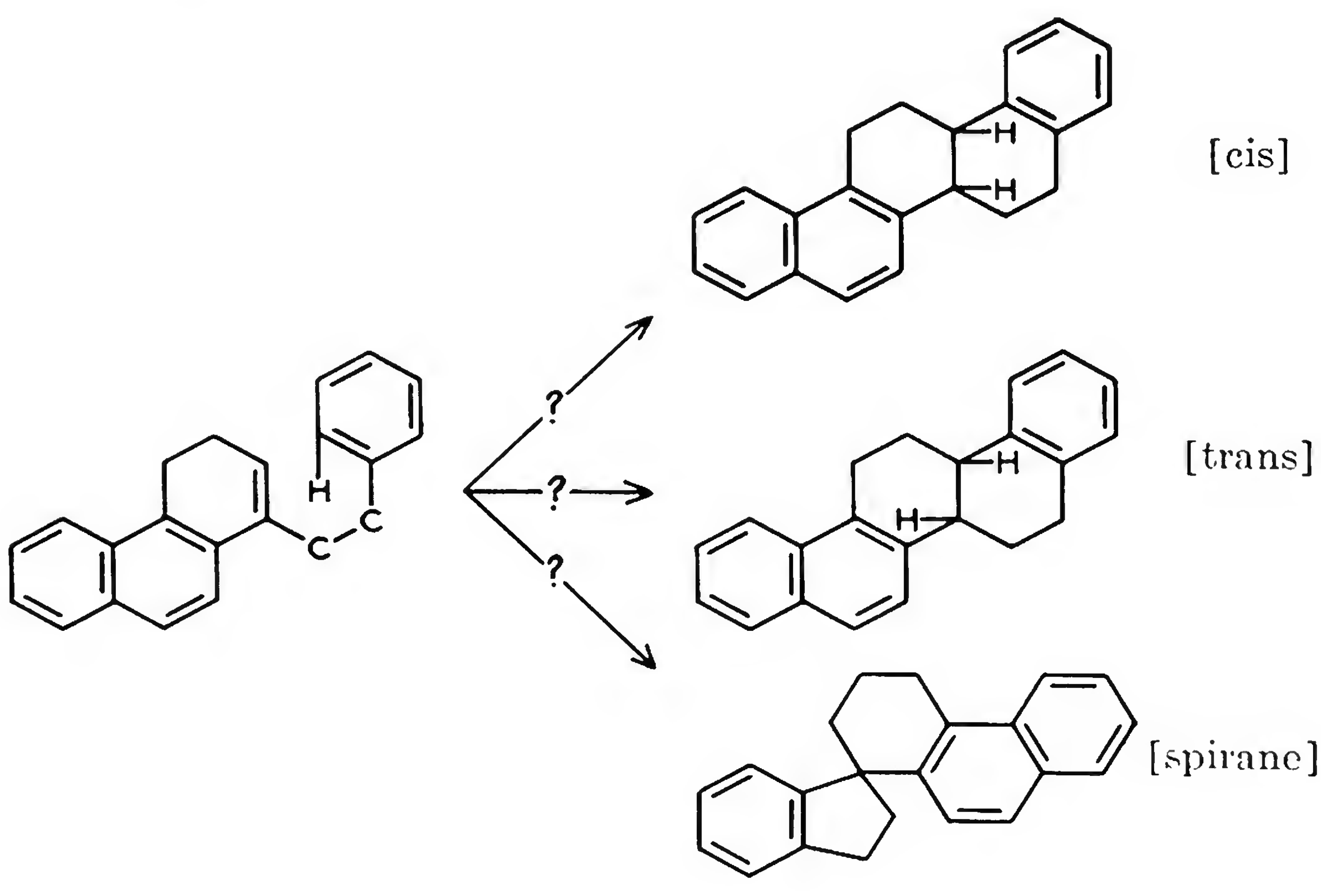
Treatment of 1-(β-phenethyl)-2-methyl-3-α-naphthindene with aluminum chloride plus carbon disulfide for 4 hours at 0° gave 60 per cent of 5,6,6a,13a-tetrahydro-13a-methyldibenzo[ag]fluorene (*i.e.*, methyltetrahydro-1,2,5,6-dibenzfluorene:[113]



A solution of 1,2-dihydro-4-(β-phenethyl)phenanthrene in carbon disulfide was treated with aluminum chloride for 12 hours at 0°, forming 61.5 per cent of 4b,5,6,12c,13,14-hexahydrobenzo[c]chrysene (*i.e.*, 3,4,4a,-9,10,10a-hexahydro-1,2,5,6-dibenzphenanthrene):[46]

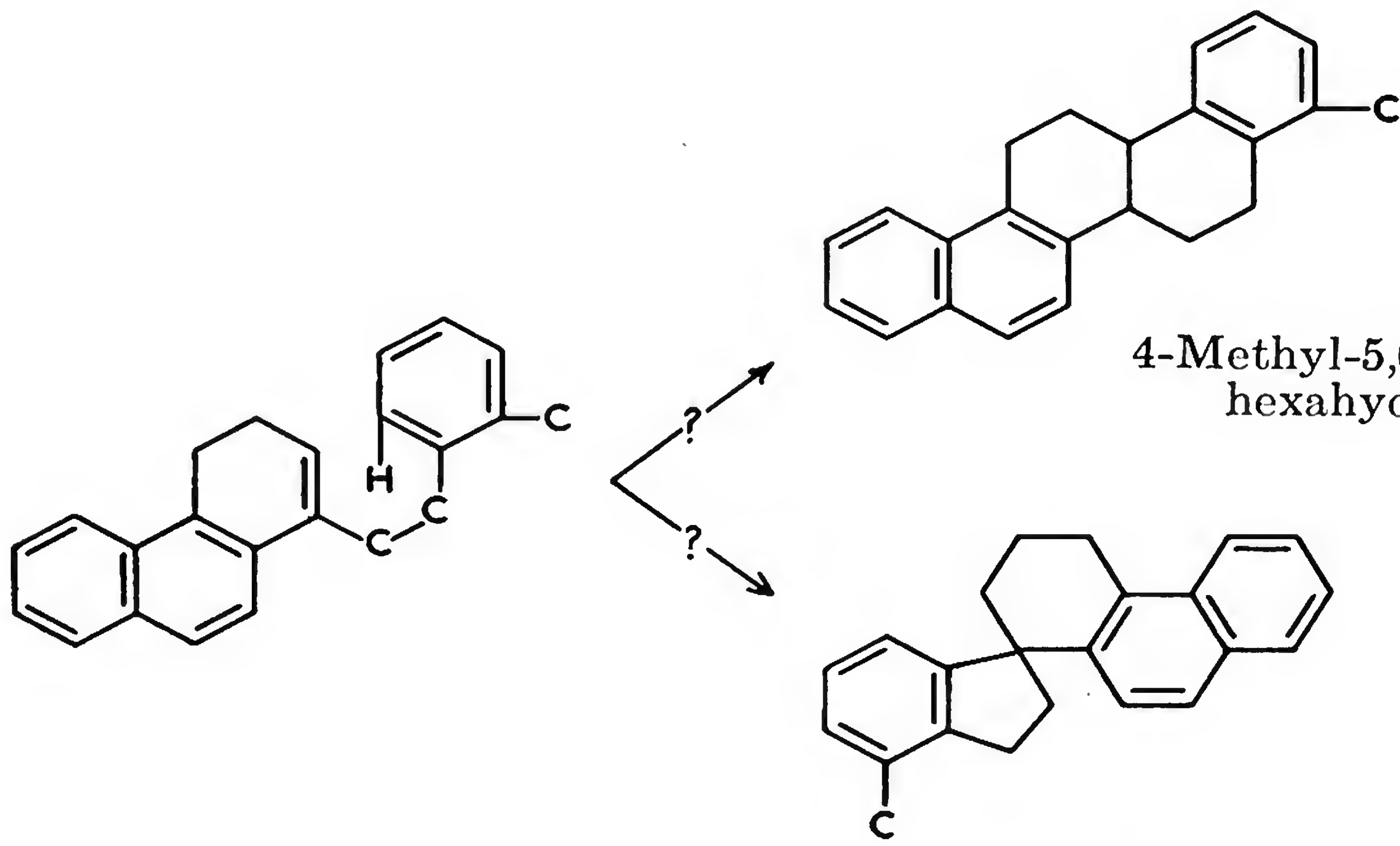


The action of aluminum chloride at 0-5° upon 1-(β-phenethyl)-3,4-dihydrophenanthrene (dissolved in carbon disulfide) probably gives a considerable amount of 3′,4′-dihydro-spiro[indan-1,1′(2′)-phenanthrene] and a small quantity of 5,6,6a,13,14,14a-hexahydropicene:[141]



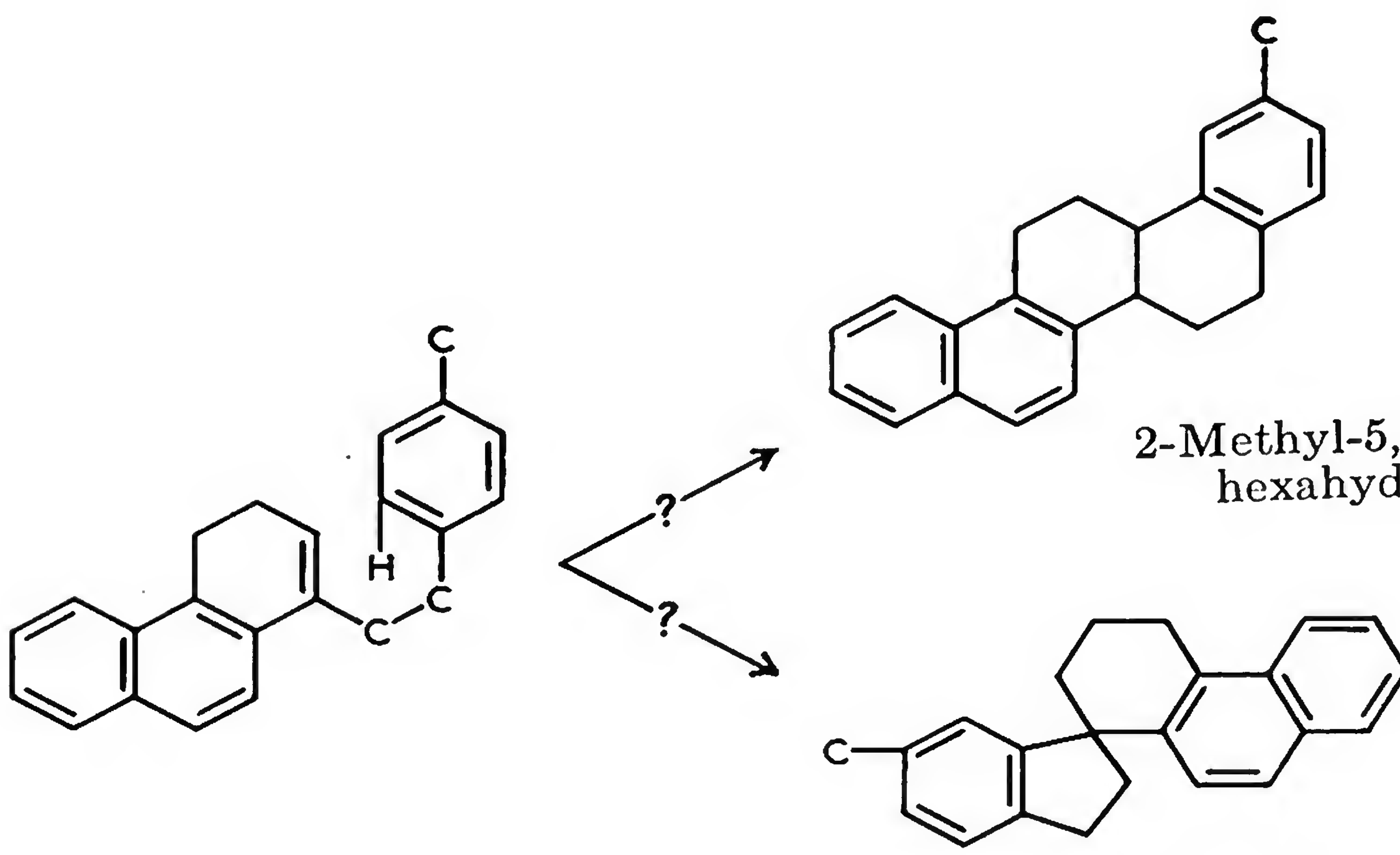
Dehydrogenation of the product over a palladium-charcoal catalyst yielded much unchanged "spirane" and only one per cent of picene. The

cyclization of 1-(β-o-tolylethyl)-3,4-dihydrophenanthrene, and of 1-(β-p-tolylethyl)-3,4-dihydrophenanthrene, in the presence of aluminum chloride plus carbon disulfide has been described.[141] The expected dehydrogenation products, 4-methylpicene and 2-methylpicene respectively, were not found after a heating of the cyclizates with a palladium-charcoal catalyst. The possible isomerizations can be formulated as follows:



4-Methyl-5,6,6a,13,14,14a-hexahydropicene

4-Methyl-3′,4′-dihydro-spiro-[indan-1,1′(2′)-phenanthrene]



2-Methyl-5,6,6a,13,14,14a-hexahydropicene

6-Methyl-3′,4′-dihydro-spiro-[indan-1,1′(2′)-phenanthrene]

The experimental data on aromatic-cyclene hydrocarbons, including calculated concentrations of catalysts and yields of products, are given in Table 42, p. 392.

Conclusions

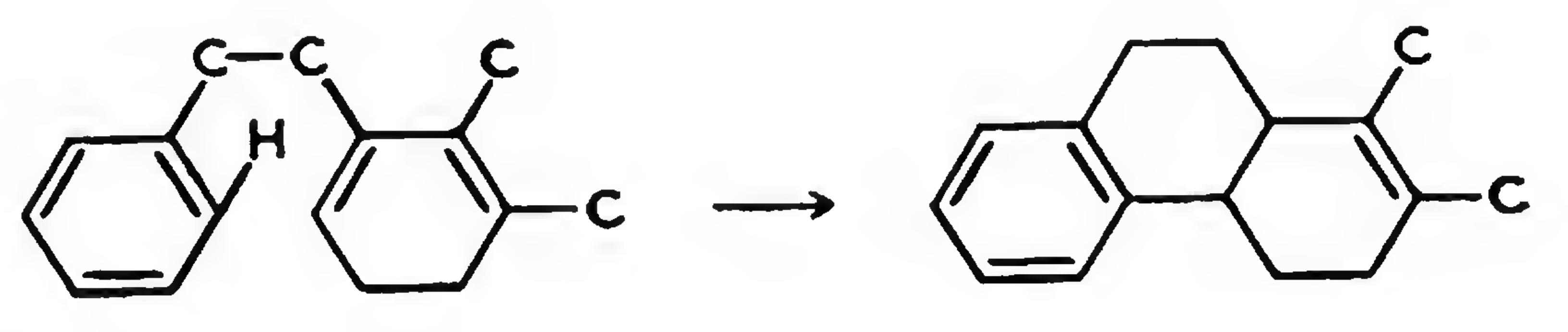
Aromatic cyclene hydrocarbons wherein a cyclene ring is attached to an aromatic ring (directly, or with one or two methylene groups in series

effecting the attachment) generally undergo cycloisomerization in the presence of such catalysts as: aluminum chloride plus carbon disulfide, stannic chloride plus hydrogen chloride and benzene, or sulfuric acid plus acetic acid.

AROMATIC-CYCLODIENE HYDROCARBONS

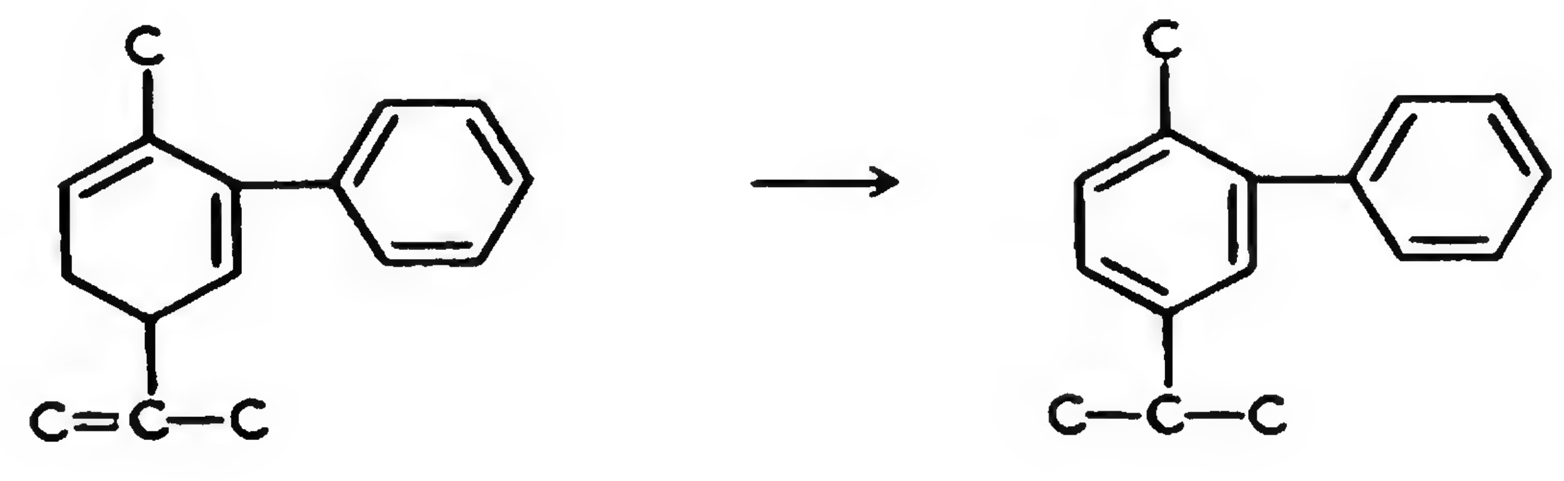
Isomerizations

Some aromatic-cyclodiene hydrocarbons can be expected to undergo cyclization in the manner of the foregoing aromatic-cyclenes. Unsaturated aliphatic side-chains apparently must be absent. 1,2-Dimethyl-3-(β-phenethyl)cyclohexadiene-1,3 was isomerized to 1,2-dimethyl-3,4,4a,-9,10,10a-hexahydrophenanthrene, *i.e.*, "1,2-dimethyl-3,4,9,10,11,12-hexahydrophenanthrene," by treatment with stannic chloride plus hydrogen chloride and benzene at 0°: [56]



Aromatic-cyclodiene hydrocarbons undergo aromatization by double-bond migration rather than by cyclization when they contain an alkenyl group attached to the cyclodiene ring. The products formed in the known examples are polyalkyl biphenyl or polyalkyl diphenylmethane. As expected, acidic catalysts are used in these isomerizations.

1-Methyl-2-phenyl-4-isopropenylcyclohexadiene-2,6, heated under reflux for 5 hours with hydrogen chloride in acetic acid, gave 1-methyl-2-phenyl-4-isopropylbenzene: [311]



"1-Methyl-2-benzyl-4-isopropenylcyclohexadiene-2,6" (which may be a mixture of 1-methyl-2-benzyl-4-isopropenyl-cyclohexadiene-3,6 and 1-methyl-2-benzal-4-isopropenyl-cyclohexene-6 [481]) undergoes an aromatization into 1-methyl-2-benzyl-4-isopropylbenzene.[310, 481] The catalyst is acetic acid containing one per cent of sulfuric acid: [481]

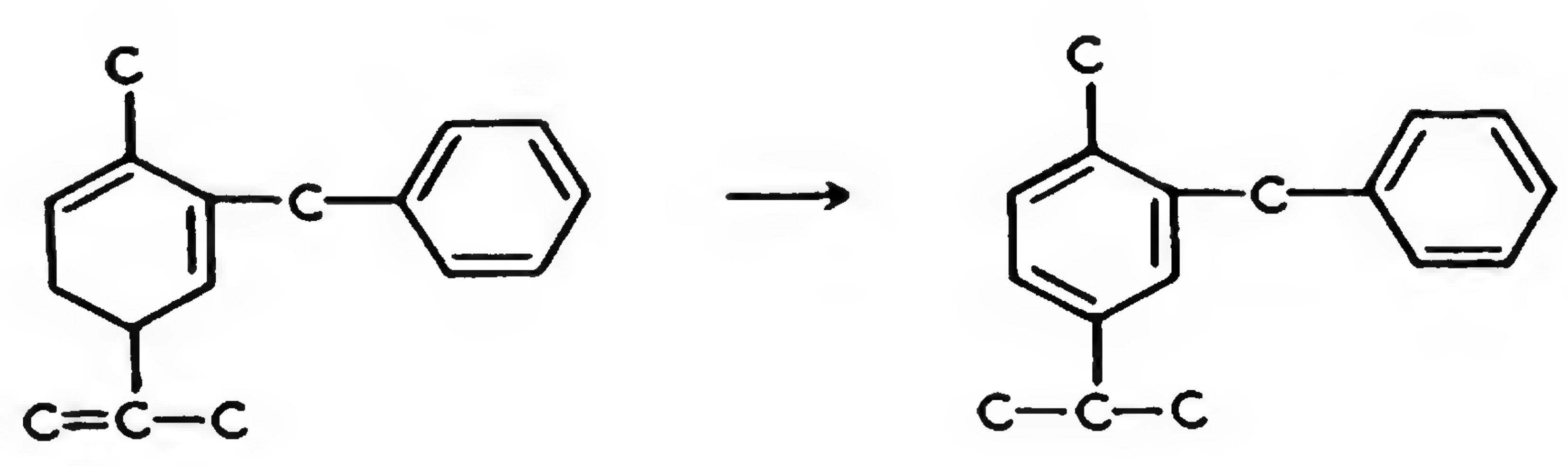


Table 43, p. 398.

Conclusions

Summary

Isomerizations were discussed for individual members of the groups: alkanes, alkenes, allenic alkadienes, non-allenic alkadienes, alkapolyenes, alkynes, alkadiynes, alkapolyynes, cyclanes, cyclanes with saturated side-chains, cyclanes with unsaturated side-chains, spiranes, bicyclanes, bicyclanes with saturated side-chains, bicyclanes with unsaturated side-chains, tricyclanes, pentacyclanes, cyclenes, cyclenes with saturated side-chains, cyclenes with unsaturated side-chains, cyclodienes with saturated side-chains, cyclodienes with unsaturated side-chains, bicyclenes, bicyclenes with saturated side-chains, bicyclenes with unsaturated side-chains, bicyclodienes with saturated side-chains, tricyclenes, tricyclenes with saturated side-chains, tricyclenes with unsaturated side-chains, tetracyclenes, pentacyclenes, alkyl benzenes, alkenyl benzenes, allenic alkadienyl benzenes, non-allenic alkadienyl benzenes, alkapolyenyl benzenes, alkynyl benzenes, indanes, indenes, fluorenes, naphthalenes, anthracenes, phenanthrenes, naphthacenes, aromatic-cyclane hydrocarbons, aromatic-cyclene hydrocarbons, and aromatic-cyclodiene hydrocarbons.

To enable the reader to make facile applications of the typical reactions that were "analyzed" in this survey, to other examples which he may encounter, it seems proper to give a few rules generally applicable in isomerization:

1. Isomerization tends to be a specific reaction. However, alkene isomerizations involving a change in branching generally develop some side products, because of the ease with which the branched alkenes are polymerized and depolymerized.

2. Isomerization has a tendency to produce a more compact structure of the molecule. Branched structures are the most compact and should have maximum stability. An equilibrium mixture of straight and branched molecules, especially, can be expected in the case of simpler structures.

3. In isomerization, systems having double bonds strive toward the attainment of conjugated positions.

4. The course of an isomerization is dependent on the reaction conditions (including catalyst effects). Sodium and sodamide generally convert an allenic alkadiene, alkyne-2, or alkyne-3 into the sodium derivative of an alkyne-1 (hydrolyzed by water to the free alkyne). Alcoholic alkalies and soda-lime convert an alkyne-1 into an allenic alkadiene or into an alkyne-2. Acidic reagents are effective catalysts

in isomerization via cyclization or via the shift of a double bond into an adjacent ring.

5. All isomerizations observed to date should proceed at least slightly in the reverse direction under proper reaction conditions. Specificity of mechanism alone does not prevent the reversibility in direction of an isomerization. In this respect, the directive action of sodium or sodamide is opposite in character to that of alcoholic alkalies or soda lime.

6. Isomerization involves changes in symmetry and saturation of molecules: (a) the *shifting* of alkyls, aryls, bicyclic bonds ("bridges"), and unsaturated bonds; (b) *contractions* and *expansions* of rings and side-chains; (c) *eliminations* and *formations* of rings, saturated or unsaturated side-chains, and of unsaturated bonds in general; and (d) the formation of geometrical (*cis-trans*) isomers.

7. Intercomparisons of the various groups of hydrocarbons indicate the prevalence of a fundamental allylic type or triad system of hydrogen migration. These comparisons should be an integral part of future experimental work on isomerization.

8. The specificity in formation of isomer products, as shown by their high yields in numerous cases, is probably the result of an advantageous change in the free energy of hydrocarbon molecules undergoing isomerization.

Last, but not least in importance, isomerization can be rigidly defined with respect to its several steps or changes in the molecule (Table 44), p. 400. The term "isomerization" should be used more specifically in the chemical literature, since the reaction is often accompanied (to a varying degree and with unknown significance) by "side reactions," such as alkylation, dealkylation, cracking, hydrogenation, dehydrogenation, or polymerization. The main reactions of alkylations, dehydration, hydration, oxidation, and reduction, in turn, can be accompanied by the formation of isomers. Therefore, a "true isomerization" or a "direct isomerization" is the formation of an isomer without the occurrence of a stable intermediate under specific reaction-conditions. "Delayed isomerization" is isomerization via stable intermediates, such as terpene hydrochlorides or the unsaturated ethers from the alkynes.

Tables of Discretization Data

Table 6. Isomeriza

Contact time	Alkane + catalyst (Reactants)	Temp.
8	n-Bu[illegible] ([illegible]%)	
1	n-Bu[illegible] ([illegible]%)	
2 months	n-Bu[illegible] ([illegible]%)	
620	n-Buta[illegible] ([illegible]%)	
192	([illegible]%)	
113	([illegible]%)	
65	([illegible]%)	
40	([illegible]%)	
(glass vessel study)		
616	n-Buta[illegible] ([illegible]%)	
193	n-Buta[illegible] ([illegible]%)	
192	n-Buta[illegible] ([illegible]%)	
114	n-Bu[illegible] ([illegible]%)	
112	n-Bu[illegible] ([illegible]%)	
64	n-Bu[illegible] ([illegible]%)	
65.5	n-Bu[illegible] ([illegible]%)	
40	n-Bu[illegible] ([illegible]%)	
40	n-Bu[illegible] ([illegible]%)	
24	88% Butane, 11% Isobutane ([illegible]%)	
23	95% Butane, Isobutane ([illegible]%)	
142	95% Butane, Isobutane ([illegible]%)	
23	95% Butane, Isobutane ([illegible]%)	
4	89% Butane, 11% Isobutane ([illegible]%)	
4	89% Bu ([illegible]%), 11% Isobu ([illegible]%)	
(anhydrous)	n-Bu[illegible] ([illegible]%) ([illegible]%)	
(anhydrous)	n-Butane + $AlCl_3$	
	HCl (anhydrous)	
	n-[illegible] $AlCl_3$ or $AlBr_3$	

tion of Alkanes

Products		Refer-
by weight on original alkane	Pressure / Other Products	ences
(5%) Isobutane	(Isomers C_7H_{16}) (measured at 25°) n-C_7H_{16}	(283)
(1.3%) Isobutane	n-Butane 2.2	(419) (422)
(8–22%) Isobutane	(Hydrogen) n-Butane 3	(384)
"Equilibrium conditions"		(366)
(15%) Isobutane	n-Butane (liquid phase)	
(15%) Isobutane	n-Butane (liquid phase)	
(15%) Isobutane	n-Butane (liquid phase)	
(15%) Isobutane	n-Butane (liquid phase)	
(15%) Isobutane	n-Butane (liquid phase)	
(9.5%) Isobutane	n-Butane bomb	(385)
(1.4%) Isobutane	n-Butane bomb	(385)
(3.0%) Isobutane	n-Butane bomb	(385)
(3.8%) Isobutane	n-Butane bomb	(385)
(4.3%) Isobutane	n-Butane bomb	(385)
(0.5%) Isobutane	n-Butane bomb	(385)
(2.2%) Isobutane	n-Butane bomb	(385)
(0.7%) Isobutane	n-Butane bomb	(385)
(2.2%) Isobutane	n-Butane bomb	(385)
Isobutane / n-Butane = 0.37	2.2 (liquid phase)	(419) (422)
Isobutane / n-Butane = 0.408	autoclave	(422)
Isobutane / n-Butane = 0.62	autoclave	(422)
Isobutane / n-Butane = 0.537	autoclave	(422)
Isobutane / n-Butane = 0.614	autoclave	(422)
Isobutane / n-Butane = 0.763	3 of HCl (measured at 20°)	(422)
Isobutane / n-Butane = 0.361	3 of HCl (measured at 20°)	(422)
(50%) Isobutane	4 of HCl (liquid phase)	(418) (422)
Isobutane	(liquid phase)	(416a)

Table 6. Isomeriza

Reactants: Alkane	Reactants: Catalyst (Per cent by weight on alkane+catalyst)	Contact Time (hours)	Temp. (°C.)
n-Butane	$AlCl_3$ (anhydrous) HCl	380 cc. Butane and 38 cc. HCl per 9.1 g. catalyst per hour	130
n-Butane	$AlCl_3$ (anhydrous) HCl	330 cc. Butane and 33 cc. HCl per 10.1 g. catalyst per hour	150
n-Butane	$AlCl_3$ Carrier (pumice or silica)		below 160 (preferably)
n-Butane	$AlCl_3$ (16.4%) HCl (2% of input-n-butane) (1.6%)	12	150
n-Butane	$AlCl_3$ (31.6%) HCl (8.3% of input-n-butane) (5.2%)	12	150
n-Butane	$AlCl_3$ (anhydrous) (31.6%) HCl (anhydrous) (5.3%)	4	175
n-Butane	$AlCl_3$+activated carbon (1 : 1) HCl (2% of input-gas)	0.8 kgm. n-butane per kgm. catalyst per hour	200
n-Butane	$AlCl_3$+activated carbon (1 : 1) prepared with the aid of HCl at 250° and 25 atmospheres' H_2 pressure HCl (2% of input-gas)	"moderate space velocity"	200
n-Butane	$AlCl_3$ (anhydrous) (16.03%) $CuSO_4 . 2HCl$ (13.97%)	2.0	70
n-Butane 89% Isobutane 11%	$AlCl_3$ Al_2O_3 (prepared partially dehydrated from $Al(OH)_3$ at 300°) The catalyst had 84.5% of $AlCl_3$ and 15.5% of Al_2O_3 by weight.	0.12 kgm. feed per liter of catalyst per hour	100
n-Butane 89% Isobutane 11%	$AlCl_3$ Al_2O_3 (prepared partially dehydrated from $Al(OH)_3$ at 300°) The catalyst had 84.5% of $AlCl_3$ and 15.5% of Al_2O_3 by weight.	90 sec. or 0.063 kgm. feed per liter of catalyst per hour	120 130 140 150
n-Butane 89% Isobutane 11%	$AlCl_3$ Al_2O_3 (prepared partially dehydrated from $Al(OH)_3$ at 300°) The catalyst had about 84.5% of $AlCl_3$ and about 15.5% of Al_2O_3 by weight. HCl (5% by weight on input-butanes)	0.4 kgm. gases per liter of catalyst per hour	100
n-Butane 91% Isobutane 9%	$AlCl_3$ Al_2O_3 (prepared partially dehydrated from $Al(OH)_3$ at 300°)	30 g. feed per 250 cc. catalyst per hour	100

tion of Alkanes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkane) Isomers		Other Products		References
1 (?)	Isobutane	(37.2%)	CH_4 n-Butane	(0.06%) (62.7%)	(382)
1 (?)	Isobutane	(42.4%)	CH_4 (?) C_3H_8 n-Butane	 (33.55%) (24.1%)	(382)
(gas phase)	Isobutane				(416b)
30	Isobutane	(66.5%)	n-Butane	(31.9%)	(604) (605)
30	Isobutane	(13.3%)	CH_4 C_2H_6 C_3H_8 Liquid hydrocarbons	(4.5%) (7.6%) (42.0%) (20.0%)	(604)
35	Isobutane	(13.3%)	H_2 CH_4 C_2H_6 C_3H_8 n-Butane Heavy brown oil	(0.07%) (4.5%) (7.7%) (42%) (10%) (20%)	(276)
44	Isobutane	(53%)	C_3H_8 n-Butane Liquid hydrocarbons	(3%) (36%) (8%)	(604)
44	Isobutane	(53%)	C_3H_8 n-Butane Liquid hydrocarbons	(3%) (36%) (8%)	(284)
sealed tube (liquid phase)	Isobutane	(48.3%)	n-Butane	(51.7%)	(382)
11	Isobutane	(55%)	n-Butane	(45%)	(165a)
1 1 1 1	Isobutane Isobutane Isobutane Isobutane (Shows temperature effect)	(38%) (38%) (43%) (50%)			(165a)
11	Isobutane	(58%)	n-Butane		(165a)
11	Isobutane (first 44 hours) Isobutane (succeeding 56 hours)	(50%) (65–57%)			(165a)

Table 6. Isomeriza

Reactants: Alkane		Reactants: Catalyst (Per cent by weight on alkane+catalyst)	Contact Time (hours)	Temp. (°C.)
		The catalyst had 87% of $AlCl_3$ and 13% of Al_2O_3 by weight. HCl (5% by weight on input-butanes and only after 44 hours' run)	during first 44 hours 60–100 g. feed per 250 cc. catalyst per hour during the succeeding 56 hours	
n-Butane Isobutane	89% 11%	$AlCl_3$ Pipe clay (partially dehydrated at 300° for 2 hours)		about 100
n-Butane Isobutane	89% 11%	$AlCl_3$ Pipe clay (partially dehydrated at 300°) The catalyst had 71.2% of $AlCl_3$ and 28.8% of pipe clay by weight.	0.13 kgm. feed per liter of catalyst per hour	120
n-Butane Isobutane	88.5% 11.5%	$AlCl_3$ (sublimed) Powdered pipe clay (partially dehydrated at 300°) The catalyst had 71.5% of $AlCl_3$ and 28.5% of pipe clay by weight.	93 sec. (one pass)	150
n-Butane Isobutane	88.5% 11.5%	$AlCl_3$ (sublimed) Powdered pipe clay (completely dehydrated at 1100°)	(one pass)	150
n-Butane Isobutane	88.5% 11.5%	$AlCl_3$ (sublimed) Kaolinite (dehydrated at 300°) The catalyst had 74.8% of $AlCl_3$ and 29.8% of kaolinite by weight.	93 sec.	150
n-Butane Isobutane	88.5% 11.5%	$AlCl_3$ (sublimed) Kaolinite (dehydrated at 1100°) The catalyst had 74.8% of $AlCl_3$ and 29.8% of kaolinite by weight.	93 sec.	150
n-Butane Isobutane	88.1% 11.9%	$AlCl_3$ Pumice The catalyst had 22.5% of $AlCl_3$ and 77.5% of pumice by weight.	20 sec.	150
n-Butane Isobutane	91% 9%	$AlCl_3$ Al_2O_3 (prepared partially dehydrated from $Al(OH)_3$ at 300°) Powdered pumice (previously dehydrated at 500°) The catalyst had 44 g. $AlCl_3$, 20 g. Al_2O_3, and 13 g. pumice.	2.5 liters feed per 77 g. catalyst per hour (one pass)	150
n-Butane Isobutane	91% 9%	$AlCl_3$ Silica gel (dehydrated at 300°) Pumice (dehydrated at 300°) The catalyst had 37 g. $AlCl_3$, 24.5 g. silica gel, and 8.5 g. pumice.	2.5 liters feed per 70 g. catalyst per hour (one pass)	150
n-Butane Isobutane	91% 9%	$AlCl_3$ Silica gel (dehydrated at 1100°) Pumice (dehydrated at 300°)	(one pass)	150
n-Butane Isobutane	91% 9%	$AlCl_3$ Sodium permutite (dehydrated at 110°) The catalyst had 53 g. $AlCl_3$ and 29 g. sodium permutite.	2.5 liters feed per 82 g. catalyst per hour (one pass)	150

tion of Alkanes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkane) Isomers		Other Products		References
about 11	Isobutane	(55%?)	*n*-Butane	(45%?)	(165a)
11	Isobutane	(61.4%)	*n*-Butane Decomposition products	(37.7%) (0.9%)	(165a)
1	Isobutane	(54%)	*n*-Butane	(46%)	(165a)
1	Isobutane	(14.5%)			(165a)
1	Isobutane	(54%)	*n*-Butane	(46%)	(420c)
1	Isobutane	(26%)	*n*-Butane	(74%)	(420c)
(gas phase)	Isobutane	(28%)	*n*-Butane	(72%)	(420b)
1	Isobutane	(42%)			(165a)
1	Isobutane	(33%)			(165a)
1	Isobutane	(1.7%)			(165a)
1	Isobutane	(20.2%)			(165a)

Table 6. Isomeriza

Reactants: Alkane		Reactants: Catalyst (Per cent by weight on alkane+catalyst)		Contact Time (hours)	Temp. (°C.)
n-Butane Isobutane	91% 9%	$AlCl_3$ Sodium permutite (dehydrated at 1100°)		(one pass)	150
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl	(31.2%) (6.3%)	4	20
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl	(31.2%) (6.3%)	4	40
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl	(31.2%) (6.3%)	4	60
n-Butane Isobutane	38% 62%	$AlCl_3$ HCl			60
n-Butane Isobutane	24.9% 75.1%	$AlCl_3$ HCl			60
n-Butane Isobutane	40.4% 57.4%	$AlCl_3$ HCl			60
n-Butane Isobutane	38.6% 58.2%	$AlCl_3$ HCl			60
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl	(31.2%) (6.3%)	4	80
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl	(31.2%) (6.3%)	4	100
n-Butane Isobutane	90% 10%	$AlCl_3$ on a carrier HCl (6% by weight of butanes)		200 g. butanes per 250 cc. solid catalyst per hour	100
n-Butane and Isobutane mixtures		$AlCl_3$ on a carrier HCl (2 mole % on butanes)		(flow experiments)	100
n-Butane Isobutane	41.4% 58.2%	$AlCl_3$ HCl			100
n-Butane Isobutane	39.3% 60.5%	$AlCl_3$ HCl			100
n-Butane Isobutane	32.0% 68.0%	$AlCl_3$ HCl			100
n-Butane Isobutane	19.4% 80.6%	$AlCl_3$ HCl			100
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl	(31.2%) (6.3%)		120
n-Butane Isobutane	38% 62%	$AlCl_3$ HCl	 (trace)		140

tion of Alkanes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkane): Isomers		Other Products		References
1	Isobutane	(5%)			(165a)
autoclave	Isobutane	(15.0%)	*n*-Butane	(85.0%)	(529a)
autoclave	Isobutane	(17.6%)	*n*-Butane	(82.4%)	(529a)
autoclave	Isobutane	(22.6%)	*n*-Butane	(77.8%)	(529a)
autoclave (liquid phase)	Isobutane $\frac{\text{Isobutane}}{n\text{-Butane}}=1.82$	(64.1%)	*n*-Butane Side products	(35.3%) (0.6%)	(529a)
autoclave (liquid phase)	*n*-Butane $\frac{\text{Isobutane}}{n\text{-Butane}}=2.16$	(31.4%)	Isobutane Side products	(67.9%) (0.7%)	(529a)
autoclave (liquid phase)	Isobutane $\frac{\text{Isobutane}}{n\text{-Butane}}=2.09$	(64.7%)	*n*-Butane Side products	(31.0%) (4.3%)	(529a)
autoclave (liquid phase)	Isobutane $\frac{\text{Isobutane}}{n\text{-Butane}}=2.03$	(62.8%)	*n*-Butane Side products	(31.9%) (5.3%)	(529a)
autoclave	"Equilibrium conditions" Isobutane	(35.1%)	*n*-Butane	(64.9%)	(529a)
autoclave	Isobutane	(62.9%)	Propane *n*-Butane Pentanes and higher	(3.8%) (29.4%) (3.9%)	(529a)
16 (gas phase)	Isobutane (12– 24 hour period) (60– 72 hour period) (120–132 hour period)	 (66.4%) (63.6%) (60.8%)	*n*-Butane (12– 24 hour period) (60– 72 hour period) (120–132 hour period) Side products (12– 24 hour period) (60– 72 hour period) (120–132 hour period)	 (28.1%) (32.7%) (36.0%) (5.5%) (3.7%) (3.2%)	(529a)
11 (gas phase)	Isobutane (from isobutane side) (from *n*-butane side) "Equilibrium conditions"	 (65.0%) (65.3%)	*n*-Butane (from isobutane side) (from *n*-butane side) Side products (from isobutane side) (from *n*-butane side)	 (25.8%) (26.1%) (9.2%) (8.6%)	(135a)
autoclave (liquid phase)	Isobutane $\frac{\text{Isobutane}}{n\text{-Butane}}=2.05$	(64.3%)	*n*-Butane Side products	(31.5%) (4.2%)	(529a)
autoclave (liquid phase)	Isobutane $\frac{\text{Isobutane}}{n\text{-Butane}}=2.23$	(66.4%)	*n*-Butane Side products	(29.8%) (3.8%)	(529a)
autoclave (liquid phase)	$\frac{\text{Isobutane}}{n\text{-Butane}}=2.05$		*n*-Butane Isobutane Side products	(30.9%) (65.5%) (3.6%)	(529a)
autoclave (liquid phase)	*n*-Butane $\frac{\text{Isobutane}}{n\text{-Butane}}=2.48$	(27.7%)	Isobutane Side products	(68.5%) (3.8%)	(529a)
autoclave	Isobutane	(16.7%)	Propane *n*-Butane Pentanes and higher	(70.5%) (10.0%) (2.8%)	(529a)
5 (H_2) (gas phase?)	$\frac{\text{Isobutane}}{n\text{-Butane}}=1.65$		*n*-Butane Isobutane Side products	(37.2%) (61.5%) (1.3%)	(529a)

Table 6. Isomeriza

Reactants: Alkane		Reactants: Catalyst (Per cent by weight on alkane+catalyst)		Contact Time (hours)	Temp. (°C.)
n-Butane Isobutane	24.9% 75.1%	$AlCl_3$ HCl	(trace)		140
n-Butane Isobutane	40.4% 57.4%	$AlCl_3$ HCl	(trace)		140
n-Butane Isobutane	38.6% 58.2%	$AlCl_3$ HCl	(trace)		140
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl	(33%)	16 2 18 4	20 70 70 100
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	4	20
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	16	20
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(24.4%) (26.3%)	16	20
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	64	20
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	16	65
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	4	80
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	5	90
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	4	100
n-Butane Isobutane	89% 11%	$AlCl_3$ HCl (anhydrous)	(31.1%) (5.9%)	4	120
n-Butane and Isobutane mixtures		$AlBr_3$ (?) or $AlCl_3$ (?)		1000 or more	10
		$AlBr_3$ (?) or $AlCl_3$ (?)			20
		$AlBr_3$ (?) or $AlCl_3$ (?)			52
		$AlBr_3$ (?) or $AlCl_3$ (?)			99
		$AlCl_3$			123
		$AlCl_3$			150
n-Butane and Isobutane mixtures		$AlCl_3+CuSO_4 . 2HCl$			70
n-Butane and Isobutane mixtures		$AlCl_3$ HCl (part of input-gas)			110
n-Butane and Isobutane mixtures		$AlCl_3$ HCl (part of input-gas)			130

tion of Alkanes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkane): Isomers	Other Products	References
5 (H$_2$) (gas phase?)	n-Butane (29.8%) $\frac{\text{Isobutane}}{n\text{-Butane}} = 2.29$	Isobutane (68.3%) Side products (1.9%)	(529a)
5 (H$_2$) (gas phase?)	Isobutane (58.1%) $\frac{\text{Isobutane}}{n\text{-Butane}} = 1.53$	n-Butane (38.1%) Side products (3.8%)	(529a)
5 (H$_2$) (gas phase?)	Isobutane (58.5%) $\frac{\text{Isobutane}}{n\text{-Butane}} = 1.82$ "Equilibrium conditions"	n-Butane (32.2%) Side products (9.3%)	(529a)
20 of HCl 4 of HCl 4 of HCl 4 of HCl (all liquid phase)	Isobutane (22.3%) Isobutane (23.5%) Isobutane (51%) Isobutane (62.9%) (yield study or disclosure)		(420d)
3–4 of HCl (liquid phase)	Isobutane (15.0% in reaction mixture)		(418)
4 of HCl (liquid phase)	Isobutane (16.8% in reaction mixture)		(418)
20 of HCl (liquid phase)	Isobutane (22.3% in reaction mixture)		(418)
4 of HCl (liquid phase)	Isobutane (21.3% in reaction mixture)		(418)
4 of HCl (liquid phase)	Isobutane (51.2% in reaction mixture)		(418)
4 of HCl (liquid phase)	Isobutane (35.0% in reaction mixture)		(418)
4 of HCl (liquid phase)	Isobutane (65.0% in reaction mixture)	Non–C$_4$ hydrocarbons (1–2%)	(418)
4 of HCl (liquid phase)	Isobutane (62.9% in reaction mixture)	Non–C$_4$ hydrocarbons (7.7%)	(418)
4 of HCl (liquid phase)	Isobutane (16.7% in reaction mixture)	Non–C$_4$ hydrocarbons (73.3%)	(418)
vapor phase 1 (?)	$\frac{\text{Isobutane}}{n\text{-Butane}} = 7.33$		(366)
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 5.06$		
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 4.21$		
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 3.00$		
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 2.33$	Propane	
vapor phase	$\frac{\text{Isobutane}}{n\text{-Butane}} = 1.86$ "Equilibrium conditions" in all 6 cases	Propane	
sealed tube (liquid phase)	$\frac{\text{Isobutane}}{n\text{-Butane}} = 3.8$ (by equation; experiments show 2.8) "Equilibrium conditions"		(382)
1 (?)	$\frac{\text{Isobutane}}{n\text{-Butane}} = 2.6$ "Equilibrium conditions"		(382)
1 (?)	$\frac{\text{Isobutane}}{n\text{-Butane}} = 2.0$ "Equilibrium conditions"	Propane ("especially when working with isobutane")	(382)

Table 6. Isomeriza

Reactants: Alkane		Reactants: Catalyst (Per cent by weight on alkane+catalyst)		Contact Time (hours)	Temp. (°C.)
n-Butane and Isobutane mixtures		$AlCl_3$ HCl (part of input-gas)			150
n-Butane and Isobutane mixtures		$AlCl_3$+KCl+ground glass HCl (part of input-gas)			180
Isobutane		$AlBr_3$	(18.9%)	2 months	27
Isobutane		$AlCl_3$ (anhydrous) HCl		320 cc. isobutane and 38 cc. HCl per 9.0 g. catalyst per hour	130
Isobutane		$AlCl_3$ (anhydrous) HCl		340 cc. isobutane and 34 cc. HCl per 10.5 g. catalyst per hour	150
Isobutane		$AlCl_3$ (anhydrous) KCl Ground glass (diluent) HCl		350 cc. isobutane and 35 cc. HCl per 38.3 g. $AlCl_3$ and 5.7 g. KCl (*i.e.*, 44 g. catalyst) per hour	180
Isobutane		$AlCl_3$ (anhydrous) $CuSO_4 . 2HCl$	(16.03%) (13.97%)	2.5	70
n-Pentane		$AlBr_3$	(7.1%)	504	0
n-Pentane		$AlBr_3$	(7.1%)	168	27
n-Pentane Isopentane	80.0% 20.0%	$AlBr_3$	(7.1%)	68	27
n-Pentane Isopentane	68.9% 31.1%	$AlBr_3$	(7.1%)	68	27
n-Pentane Isopentane	60.0% 40.0%	$AlBr_3$	(7.1%)	68	27
n-Pentane		$AlBr_3$ (anhydrous)	(9.7%)	95	room
n-Pentane		$AlCl_3$ (freshly sublimed)		several days	b. p.
n-Pentane		$AlCl_3$ (freshly sublimed)			40–133
n-Pentane		$AlCl_3$ H_2O	(22.9–28.3%) (0.6–0.8%)	5–10 days	b. p.
n-Pentane		$AlCl_3$ (lump or powder)	(33.3%)	20	23.9
n-Pentane		$AlCl_3$ H_2O	(32.9%) (1.3%)	20	23.9
n-Pentane		$AlCl_3$ HCl	(8.9%) (1.8%)	20	23.9
n-Pentane		$AlCl_3$ HCl	(32.9%) (1.3%)	20	23.9

...tion of Alkanes—*Continued*

Products (Per cent by weight on original alkane)	Reference	Other Products
Propane (especially when working with isobutane)		
Isobutane		
n-Butane "Equilibrium conditions"	(382)	
Propane (especially when working with isobutane)		
Isobutane		
n-Butane "Equilibrium conditions"	(382)	
Isobutane (18–22%) *n*-Butane "Equilibrium conditions"	(382)	
(23.4%) *n*-Butane (76.4%) Isobutane	1 (?)	
(15.9%) *n*-Butane (0.06%) [illegible] (5[illegible]%) (27.[illegible]%) Isobutane	(382) 1 (?)	
(27.4%) *n*-Butane (1.5%) [illegible] (6[illegible].1%) Isobutane	(382) 1 (?)	
(20.4%) *n*-Butane (79.6%) Isobutane	(382) sealed tube (liquid phase)	
Alkanes other than pentanes ([illegible]%) Isopentane (0.7%?)	1	
Alkanes other than pentanes (20[illegible]%) Isopentane (7.1%?)	(385) 1	
Alkanes other than pentanes (30[illegible]%) Isopentane (4.9%?)	(385) 1	
Alkanes other than pentanes (10[illegible]%) Isopentane (8.2%?)	(385) 1	
Alkanes other than pentanes ([illegible]%) Isopentane (0.8%?)	(385) 1	
Butanes (mostly isobutane) Isopentane (3.6%)	(216) 1	
Saturated higher-boiling products (3.4%)		
Insoluble unsaturated polymer (0.5%)		
n-Pentane (unchanged) No isomers	(216) 1	
n-Pentane (unchanged) No isomers	(216) 1	

Table 6. Isomeriza

Reactants: Alkane	Reactants: Catalyst (Per cent by weight on alkane+catalyst)	Contact Time (hours)	Temp. (°C.)
n-Pentane	$AlCl_3$ with any of the following: HBr (anhydrous) HCl (anhydrous) $AlCl_3$ (hydrated) Alkyl chlorides		b. p.
n-Pentane	$AlCl_3$ with either: HBr (anhydrous) (2.5%) H_2O (2.5%)		40
n-Pentane	$AlCl_3$ (5–10% by weight of *n*-pentane) HCl (0.1–1% by weight of *n*-pentane)	4–5 days at or 0.5 hour at	room 200
n-Pentane	$AlCl_3$ on inert carriers such as: Activated carbon Silica Fuller's earth Fire-brick HCl (below 2% by weight of *n*-pentane)	continuous operation	room-200
n-Pentane	$AlCl_3$ (45%) HCl (9.9%)	3	room
n-Pentane	$AlCl_3$ (about 45%) HCl (about 9.9%)	about 2	about 26
n-Pentane	$AlCl_3$ (anhydrous) (9.0%) HCl (gas) (0.9%)	3	100
n-Pentane	50% $AlCl_3$+50% activated carbon base HCl (1% of input-gas)	1 part *n*-pentane per 1.2 parts by weight of $AlCl_3$ + active carbon per hour	200
n-Pentane	$AlCl_3$ on activated carbon HCl (1% of input-gas)	continuous operation	200
n-Pentane	$AlCl_3$ (44.6%) HCl (9.8%) $ClSO_3H$ (1.0%)	2	26
n-Pentane	$AlCl_3$ (44.6%) HCl (9.8%) FSO_3H (0.9%)	3	room
n-Pentane	$AlCl_3$ (43.1%) HCl (9.5%) FSO_3H (4.3%)	about 3	room
n-Pentane	$AlCl_3$ (8.8%) BF_3 (below 2.7%)	20	23.9
n-Pentane	$AlCl_3$ (32.7%) BF_3 (below 1.9%)	20	23.9
n-Pentane	$2AlCl_3 . 1BF_3$ (yellow complex) (9.1%)	20	26.7
n-Pentane	$AlCl_3$ (8.33%) $CuSO_4 . 2HCl$ (8.33%)	4.5	50
n-Pentane	$2AlCl_3 . 1C_6H_5(tert\text{-}C_4H_9)$ (this liquid complex contains 66% of combined $AlCl_3$, 40 cc. were used for 100 g. of pentane feed)	2.5 at and 18 at	35 120

tion of Alkanes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkane): Isomers		Other Products		References
1	Isopentane	(large %)	Butanes Saturated higher-boiling products Insoluble unsaturated polymer		(216)
1 (N_2)	Isopentane	(about 13.4%)	H_2 *n*-Butane Isobutane Higher-boiling products	(traces) (about 3%) (about 30%)	(216)
over 10	Isopentane	(60% per cycle) (90% with recycle)			(603)
over 10	Isopentane				(603)
13.6–14.3 (HCl)	Isopentane	(60%)	*n*-Pentane	(9%)	(357a)
HCl	Isopentane	(about 66%)	*n*-Pentane	(26%)	(357a)
5 (measured at 20°)	Isopentane	(30%)	Isobutane *n*-Pentane Higher hydrocarbons	(30%) (30%) (10%)	(603)
30	Isopentane	(27% per pass) (80% with recycle)	*n*-Butane Isobutane	(3.5% by vol.) (3.5% by vol.)	(603)
30	Isopentane	(27% per pass) (80% with recycle)			(605)
13.6–14.3 (HCl)	Isopentane	(65%)	C_4 and C_6 hydrocarbons *n*-Pentane	(3%) (32%)	(357a)
13.6–14.3 (HCl)	Isopentane	(81%)	C_4, C_6, and heavier hydrocarbons *n*-Pentane	(small %) (9%)	(357a)
13.6–14.3 (HCl)	Isopentane	(62%)	*n*-Pentane	(5%)	(357a)
autoclave	Isopentane	(26%)	"Butane"	(2%)	(37a)
autoclave	Isopentane	(70%)	"Butane"	(2%)	(37a)
autoclave	Isopentane	(40%)	"Butane"	(12%)	(37a)
sealed tube (liquid phase)	Isopentane $\frac{\text{Isopentane}}{n\text{-Pentane}} = 4.40$	(21.7%)	*n*-Butane Isobutane *n*-Pentane High-boiling fraction	(7.5%) (27%) (4.93%) (26%)	(382a)
1 (?)	Isopentane	(18.3%)	Isobutane *n*-Pentane	(8.7%) (73.0%)	(420a)

Table 6. Isomeriza

Reactants: Alkane		Reactants: Catalyst (Per cent by weight on alkane+catalyst)		Contact Time (hours)	Temp. (°C.)
n-Pentane		$2AlCl_3 . 1C_6H_5(tert\text{-}C_4H_9)$ (30 cc. of this liquid complex were used for 100 g. of pentane feed) $AlCl_3$ (also used, 30 g. for 100 g. of pentane feed)		120	120
n-Pentane		$ZrCl_4$ (anhydrous) HCl (gas)	(22.4%)	3	150
Isopentane		$AlBr_3$	(7.1%)	504	0
Isopentane *n*-Pentane	90.0% 10.0%	$AlBr_3$	(7.1%)	240	0
Isopentane *n*-Pentane	85.0% 15.0%	$AlBr_3$	(7.1%)	240	0
Isopentane		$AlBr_3$	(9.09%)	19 days	25
Isopentane *n*-Pentane	70% 30%	$AlBr_3$	(9.09%)	55 days	25
Isopentane		$AlBr_3$	(7.1%)	168	27
Isopentane *n*-Pentane	70.8% 29.2%	$AlBr_3$	(7.1%)	68	27
Isopentane *n*-Pentane	60.8% 39.2%	$AlBr_3$	(7.1%)	68	27
Isopentane *n*-Pentane	70% 30%	$AlCl_3$ HCl (anhydrous)	(9.09%) (?%)	4.0	70
Isopentane *n*-Pentane	85% 15%	$AlCl_3$ HCl (anhydrous)	(9.09%) (?%)	4.0	70
Isopentane *n*-Pentane	95.5% 4.1%	$AlCl_3$ HCl	(8.33%) (8.33%)	24	80
Isopentane *n*-Pentane	87.5% 12.0%	$AlCl_3$ HCl	(8.33%) (8.33%)	24	80
Isopentane *n*-Pentane	79.7% 19.9%	$AlCl_3$ HCl	(8.33%) (8.33%)	24	80
Isopentane *n*-Pentane	68% 32%	$AlCl_3$ HCl (anhydrous)	(9.09%) (?%)	2.5	90
Isopentane		$AlCl_3$ $CuSO_4 . 2HCl$	(8.33%) (8.33%)	4.5	50

...ion of Alkanes—Continued

Products	Refer-ence
[illegible]	[illegible]

Table 6. Isomeriza

Reactants: Alkane		Reactants: Catalyst (Per cent by weight on alkane+catalyst)		Contact Time (hours)	Temp. (°C.)
Isopentane		$AlCl_3$	(8.33%)	1.3	90
		$CuSO_4 \cdot 2HCl$	(8.33%)		
Isopentane	70%	$AlCl_3$	(8.33%)	1.5	90
n-Pentane	30%	$CuSO_4 \cdot 2HCl$	(8.33%)		
Isopentane	80%	$AlCl_3$	(8.33%)	1.5	90
n-Pentane	20%	$CuSO_4 \cdot 2HCl$	(8.33%)		
Tetramethylmethane		$AlBr_3$	(16.3–29.1%)	2300	room
n-Hexane		Cu tube		25 sec.	609
n-Hexane		Glass tube		6	420
n-Hexane		Glass tube		1	450
n-Hexane		SiO_2	(10%)	100	370
		Glass tube			
n-Hexane		SiO_2	(10%)	6	420
		Glass tube			
n-Hexane		MoS_2	(10%)	6	420
		Glass tube			
n-Hexane		MoS_2	(20%)	2	400
		Steel autoclave			
n-Hexane		$AlBr_3$	(5.9–8.7%)		room
n-Hexane		$AlCl_3$	(3%)	1.5	77–80
		Propyl bromide			
n-Hexane		$AlCl_3$	(3%)	3	77–80
		Propyl bromide			
n-Hexane		$AlCl_3$	(5%)	1.5	80
n-Hexane		$AlCl_3$	(5%)	1	90
n-Hexane		$AlCl_3$	(4%)	2	90
n-Hexane		$AlCl_3$	(4%)	3	90
n-Hexane		$AlCl_3$	(5%)	1	90
		Propyl chloride	(3%)		
n-Hexane		$AlCl_3$	(5%)	2	90
		Propyl chloride	(3%)		
n-Hexane		$AlCl_3$	(5%)	1	45
		Propyl chloride	(3%)		
n-Hexane		$AlCl_3$	(5%)	3	45
		Propyl chloride	(3%)		
n-Hexane		$AlCl_3$	(9.09%)	2 (?)	40
n-Hexane		$AlCl_3$	(9.09%)	2	80
n-Hexane		$AlCl_3$	(9.09%)	2 (?)	100
n-Hexane		$AlCl_3$	(9.09%)	2 (?)	120
n-Hexane		$AlCl_3$	(27.0%)	7.5	68–100
		H_2O	(1.0%)		
n-Hexane		$AlCl_3$	(9.0%)	3	69–72
		HCl	(1.0%)		
n-Hexane		$AlCl_3$		16	80
		HCl			
2-Methylpentane		$AlBr_3$	(5.9–8.7%)		room
2-Methylpentane		$AlCl_3$		16	80
		HCl			
2-Methylpentane		(96%) H_2SO_4+(4%)H_2O		500	

tion of Alkanes—Continued

Products

Per cent by weight on original alkane

Isomerization / Other Products

Isopentane

n-Pentane

boiling fraction

Isopentane

n-Pentane

Isopentane

n-Pentane

No isomers

Saturated product

2-Methylpentane

3-Methylpentane

sealed tube

liquid phase

n-Hexane

2-Methylpentane

3-Methylpentane

Table 6. Isomeriza

Reactants: Alkane	Reactants: Catalyst (Per cent by weight on alkane+catalyst)	Contact Time (hours)	Temp. (°C.)
3-Methylpentane	$AlBr_3$ (5.9–8.7%)		room
3-Methylpentane	(96%) H_2SO_4+(4%)H_2O	500	
2,2-Dimethylbutane	$AlBr_3$ (5.9–8.7%)		room
2,2-Dimethylbutane	$AlCl_3$ HCl	0–16	80
2,2-Dimethylbutane	97% H_2SO_4+3% H_2O	2.5	50 (?)
2,3-Dimethylbutane	$AlBr_3$ (5.9–8.7%)		room
2,3-Dimethylbutane	$AlCl_3$ HCl	16	80
n-Heptane	$AlCl_3$ (26.5%) H_2O (1.0%)	24	100
n-Heptane	$AlCl_3$ Ethyl chloride (experiment No. 1) Propyl chloride (experiment No. 2) Isopropyl chloride (experiment No. 3) Butyl chloride (experiment No. 4)		room
n-Heptane	$AlCl_3$ (9.2%) HCl (?%)	5	40
n-Heptane	$AlCl_3$ (9.09%)	2 (?)	40
n-Heptane	$AlCl_3$ (9.09%)	2 (?)	80
n-Heptane	$AlCl_3$ (4.76%)	2 (?)	100
n-Heptane	$AlCl_3$ (9.09%)	2 (?)	100
n-Heptane	$AlCl_3$ (13.0%)	2 (?)	100
n-Heptane	$AlCl_3$ (9.09%)	2 (?)	120
n-Heptane	$AlCl_3$ (9.09%)	2 (?)	140
n-Heptane	$AlCl_3$ (38.7%)		96
n-Heptane	$AlCl_3$ (1%)	3	220
n-Heptane	$AlCl_3$		100

...tion of Alkanes—*Continued*

Products

...by weight on original alkane

Isomers | Other Products

2-Methylpentane
liquid phase
2-Methylpentane
3-Methylpentane
2-Methylpentane
liquid phase
2,3-Dimethylbutane
No isomers
Cracking products
(H_2)
(liquid phase)
Isopentane
Dimethylbutane
Higher - boiling hydrocarbons
2-Methylpentane
liquid phase
Dimethylbutane
Hydrogen chloride
Propane
Isobutane
Pentane and hexane fractions
High-boiling cyclanes
Unsaturated hydrocarbons
Methylhexane
Dimethylpentane
from combined experiments

n-Pentane
n-Hexane
Isopentane
Isohexanes
n-Heptane
Higher n-alkanes
Higher isoalkanes
Coke
n-Heptane
n-Heptane
n-Heptane
n-Heptane
n-Heptane

Table 6. Isomeriza

Reactants: Alkane	Reactants: Catalyst (Per cent by weight on alkane+catalyst)	Contact Time (hours)	Temp. (°C.)
n-Heptane	$ZnCl_2$ (5%)	6	300
n-Heptane	$ZnCl_2$ (5%)	7	400
n-Heptane	MoS_3 (5%) CuO (5%)	7	400
n-Heptane	MoS_2 (9.0%)	2	400
n-Heptane (not pure)	MoS_3 (5%)	3	420
n-Heptane (not pure)	MoS_3 (5%)	7	420
n-Heptane (not pure)	MoS_3 (5%)	14	420
2,4-Dimethylpentane	97% H_2SO_4+3% H_2O	2	50
n-Octane	Activated-carbon	5–6 drops feed per min. (3 passes)	300–310
n-Octane	20% Pt+80% activated-carbon	5–6 drops feed per min. (3 passes)	300–310
n-Octane	Unlined steel apparatus No. 1	2	450
n-Octane	Ag-lined steel apparatus No. 1	2	325
n-Octane	Ag-lined steel apparatus No. 1	2	450
n-Octane	Ag-lined steel apparatus No. 1	2	450
n-Octane	Ag-lined steel apparatus No. 1	3.7	450
n-Octane	Steel autoclave	2.15	475
n-Octane	Cu tube	2.6 min.	591
n-Octane	23% Ni+77% Al_2O_3	5–6 drops feed per min. (3 passes)	300–310
n-Octane	21% Ni+79% ZnO	5–6 drops feed per min. (3 passes)	300–310
n-Octane	Al_2O_3	5–6 drops feed per min. (3 passes)	300–310
n-Octane	Al_2O_3	6 cc. feed per hour	300–310
n-Octane	MoS_3 (5%)	3	410
n-Octane	MoS_3 (5%)	3	440
n-Octane	Durax-glass bomb tube	24	280
n-Octane	Porcelain tube used	1/12 drop feed per sec.	450

...tion of Alkanes—*Continued*

		Products	
		Per cent by weight on original alkane	
	Pressure	Other Products	Isomers
	140 (N_2)	(407)	Isomers (11%)
	140 (H_2)	(437)	Isomers
Recovered n-heptane (85.0%)			
Higher-boiling products			
Recovered n-heptane (74.0%)		(437)	Isomers
Higher-boiling products			
Recovered n-heptane (69.0%)		(437)	Isomers
Higher-boiling products			
2,3-Dimethylpentane	1 (H_2)	(956) (659)	(15%) Isomers (4.1%)
	1 (H_2)	(659)	Isomers (15%)
Gases 123 Liquids		(380)	Isomers (11%)
Gases 74 Liquids		(380)	No isomers
Gases 60 Liquids		(380)	Isomers (16%)
Gases 99 Liquids		(380)	Isomers (17%)
Gases 201 Liquids		(380)	Isomers (19%)
Gases 70 Liquids		(380)	Isomers (10%)
Gases 1 Liquids		(380)	No isomers
	1 (H_2)	(659)	Isomers (3.5%)
Aromatics below 1%	(H_2)	(659)	Isomers
Combined ... about 5% aromatics		(659)	Isomers

Table 6. Isomeriza

Reactants: Alkane	Reactants: Catalyst (Per cent by weight on alkane+catalyst)		Contact Time (hours)	Temp. (°C.)
n-Octane	Porcelain tube used		1/12 drop feed per sec.	500
n-Octane	Porcelain tube used		1/13 drop feed per sec.	550
n-Octane	$AlBr_3+HBr$	(20%)	120	room
n-Octane	$AlCl_3$ HCl	(10%)	1.5	20
n-Octane	$AlCl_3$ Propyl chloride	(8%) (4%)	1	20
n-Octane	$AlCl_3$ HCl	(10%)	4	20
n-Octane	$AlCl_3$ $PbSO_4 . 2HCl$	(10%) (10%)	22	20
n-Octane	$AlCl_3$ HCl	(10%)	6	20
n-Octane	$AlCl_3$	(10%)	8	20
n-Octane	$AlCl_3$ HCl	(5%)	22	20
n-Octane	$AlCl_3$ $PbSO_4 . 2HCl$	(10%)	22	20
n-Octane	$AlCl_3$ HCl	(10%)	24	20
n-Octane	$AlCl_3$ HCl	(10%)	96	20
n-Octane	$AlCl_3+HCl$	(20%)	140	room
n-Octane	$AlCl_3$ HCl	(9.09%) (?%)	6	50–55
n-Octane	$AlCl_3$	(9.09%)	2 (?)	40
n-Octane	$AlCl_3$	(9.09%)	2	80
n-Octane	$AlCl_3$	(4.76%)	2 (?)	100
n-Octane	$AlCl_3$	(9.09%)	2 (?)	100
n-Octane	$AlCl_3$	(13.0%)	2 (?)	100
n-Octane	$AlCl_3$	(9.09%)	2 (?)	120
n-Octane	$AlCl_3$	(9.09%)	2 (?)	140
n-Octane	$AlCl_3$	(5%)	3	405–410
n-Octane	$ZnCl_2$	(5%)	3	410

...tion of Alkanes—*Continued*

Products

...by weight on original alkane

Pressure (atm.) | Ref. | Other Products

H_2
Alkane (C₁–C₄)
C_2H_4
Propene
(Total of 3.5 liters per 40 g. feed)

Isomers (6.43% ... 123–127%)

H_2
Alkane (C₁–C₄)
C_2H_4
Propene
(Total of 10.27 liters per 40 g. feed)

Isomers (6.46% ... 123–127%)

Pressure (atm.)	Ref.	Products
1	(374) (379)	Isomers (4.7%) Isomers (5%)
sealed tube	(379)	Isomers (13%)
1	(379)	Isomers (15.0%)
1	(379)	Isomers (17.5%)
1	(379)	Isomers (19.0%)
1	(379)	Isomers (24.0%)
1	(379)	Isomers (24.0%)
1	(379)	Isomers (24.3%)
1	(379)	Isomers (33.0%)
1	(379)	Isomers (61.0%)
1	(374)	Isomers (12.8%)
	(546a)	Isomers (17.2%)

(0.05%) Butane
(0.47%) Isopentane
(2.0%) n-Hexane
(1.0%) Isohexanes
(2.1%) n-Heptane
(1.0%) Isoheptanes
(43.0%) Octane
(0.2%) Higher n-alkanes
(4.7%) Higher isoalkanes
(0.5%) Other | 1 | (39a) | Isomers (4.75%)
(90%) n-Octane
(Pt) "Pt"... | (39a) | Isomers (24.3%)
(5%) n-Octane

Table 6. Isomeriza[illegible]

Contact Time (hours)	Temp. (°C)	alkane + catalyst weight [illegible]	
2 (?)	[illegible]	(9.0%)	2-Methylheptane
2 (?)	[illegible]	(9.0%)	2-Methylheptane
2 (?)	[illegible]	(4.5%)	2-Methylheptane
2 (?)	[illegible]	(9.0%)	2-Methylheptane
2 (?)	[illegible]	(1[illegible]%)	2-Methylheptane
2 (?)	[illegible]	(9.0%)	2-Methylheptane
2 (?)	[illegible]	(9.0%)	2-Methylheptane
2 (?)	[illegible]	(9.0%)	2,2,4-Trimethylpentane
2 (?)	[illegible]	(9.0%)	2,2,4-Trimethylpentane
2 (?)	[illegible]	(4.5%)	2,2,4-Trimethylpentane
2 (?)	[illegible]	(9.0%)	2,2,4-Trimethylpentane
2 (?)	[illegible]	(1[illegible]%)	2,2,4-Trimethylpentane
2 (?)	[illegible]	(9.0%)	2,2,4-Trimethylpentane
2 (?)	[illegible]	(9.0%)	2,2,4-Trimethylpentane
cc. feed per hour (3–4 passes)	350	$Ni + Al_2O_3$	n-Decane

tion of Alkanes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkane) Isomers		Other Products		References
1	No isomers		Gas 2-Methylheptane	(trace) (96%)	(39a)
over 1	Isomers	(2.9%)	Gas 2-Methylheptane	(3%) (55%)	(39a)
over 1	Isomers	(4.1%)	Gas 2-Methylheptane	(3.4%) (38%)	(39a)
over 1	Isomers	(4.0%)	Gas 2-Methylheptane	(3.5%) (36%)	(39a)
over 1	Isomers	(6.0%)	Gas 2-Methylheptane	(3.7%) (34%)	(39a)
over 1	Isomers	(13%)	Gas 2-Methylheptane	(4.7%) (25%)	(39a)
over 1	Isomers	(16%)	Gas 2-Methylheptane	(4.9%) (19%)	(39a)
over 1	Isomers	(4.5%)	Gas 2,2,4-Trimethylpentane	(1.5%) (85%)	(39a)
over 1	Isomers	(6.5%)	Gas 2,2,4-Trimethylpentane	(2.7%) (58.7%)	(39a)
over 1	Isomers	(10.5%)	Gas 2,2,4-Trimethylpentane	(4.0%) (42.0%)	(39a)
over 1	Isomers	(12.9%)	Gas 2,2,4-Trimethylpentane	(4.0%) (38.6%)	(39a)
over 1	Isomers	(12.7%)	Gas 2,2,4-Trimethylpentane	(3.9%) (38.1%)	(39a)
over 1	Isomers	(13.6%)	Gas 2,2,4-Trimethylpentane	(4.6%) (31.8%)	(39a)
over 1	Isomers	(15.0%)	Gas 2,2,4-Trimethylpentane	(4.8%) (27.8%)	(39a)
1 (N_2)	Isomers	(1.6%)	Hydrogen Methane *n*-Decane Aromatics	 (44%) (6.0%)	(319)

Table 10. Isomeriza

Reactants: Alkene		Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Propene				400–405
Propene				410
Propene			59–105 min.	600
Butene-1		Quartz tube		550
Butene-1		Quartz tube	100 vols. feed per vol. reaction-space per hour	550
Butene-1			100 vols. feed per vol. reaction-space per hour	400–600 (preferably 575)
Butene-1				650
Butene-1				700
Butene-1		Ni H_2 (quantity equal to butene-1)	19 min.	133
Butene-1		CaO	100 vols. feed per vol. reaction-space per hour	400–500
Butene-1		CaO Porcelain tube used		420
Butene-1		CaO Porcelain tube used	100 vols. feed per vol. reaction-space per hour	420
Butene-1		Bauxite SiO_2 TiO_2 Difficultly-reducible metal oxides Borates Phosphates Silicates (used individually)		400
Butene-1		Difficultly-reducible metal oxides Neutral borates Neutral phosphates Neutral silicates (used individually)	100 vols. feed per vol. reaction-space per hour	400–500
Butene-1		Aluminum phosphate on pumice		400
Butene-1		Aluminum phosphate on pumice (Bauxite may also be employed)	100 vols. feed per vol. reaction-space per hour	400
Butene-1		Aluminum phosphate		427
Butene-1		Aluminum sulfate		270–290
Butene-1		75% $ZnCl_2$+25% H_2O		100
Butene-1		75% $C_6H_5SO_3H$+25% H_2O		76
Butene-1		71% $HClO_4$+29% H_2O		21
Butene-1		H_3PO_4		78
Butene-1		H_3PO_4		135
Butene-1		H_3PO_4 on diatomaceous earth	206 sec.	249
cis-Butene-2	(47.2%)	"Pyrex" reaction-vessel	500 min.	347 or 390
trans-Butene-2	(52.8%)			
cis-Butene-2	(38.0%)			650

tion of Alkenes

Pressure (atms.)	Products (Per cent by weight on original alkene) Isomers		Other Products		References
	Cyclopropane				(166)
	Cyclopropane	(about 60%)			(203)
1	No isomer		Propene		(590)
			Polymers		
	Butene-2	(87%)	Butene-1	(11%)	(266)
			Polymer	(2%)	
1	Butene-2	(87%)	Butene-1	(11%)	(267)
			Polymer		
1	Butene-2				(267)
	cis-Butene-2	(4.4%)	Butene-1	(43.4%)	(264)
	trans-Butene-2	(7.1%)			
	Butene-2	(2.4%)	Butene-1	(12.7%)	(264)
	Butene-2		*n*-Butane	(10%)	(600)
1	Butene-2				(267)
	Butene-2	(92%)	Polymer		(266)
1	Butene-2	(92%)	Polymer		(267)
	Butene-2				(266)
1	Butene-2				(267)
	Butene-2	(almost 100%)			(266)
1	Butene-2	(almost 100%)			(267)
1	Butene-2	(70–80%)	Butene-1	(20–30%)	(285)
1	Butene-2				(212)
1	Butene-2	(5%)			(285)
1	Butene-2	(13%)			(285)
1	Butene-2	(21%)			(285)
1	Butene-2	(12%)	Butene-1	(88%)	(285)
1	Butene-2	(60%)	Butene-1	(40%)	(285)
7.8	Butene-2	(100%)			(285)
sub-atm.	*cis*-Butene-2	(47.2%)			(307)
	trans-Butene-2	(52.8%)			
	Butene-1	(10.7%)	*cis*-Butene-2	(22.0%)	(264)

Table 10. Isomeriza

Reactants: Alkene		Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
trans-Butene-2 *cis*-Butene-2	(62.0%) (38.0%)			700
trans-Butene-2 *cis*-Butene-2	(62.0%)	H_3PO_4		100
n-Butenes (various mixtures with more than or less than 96 per cent of Butene-2)		Ni wire of 0.1 mm. diameter H_2		76
Butene-1 Butene-2	(15.2%) (83.8%)	Activated SiO_2–Al_2O_3	525 cc. feed per cc. catalyst per hour	385
Butene-1 Butene-2	(15.2%) (83.8%)	Activated SiO_2–Al_2O_3	200 cc. feed per cc. catalyst per hour	400
Butene-1 Butene-2	(15.2%) (83.8%)	Activated SiO_2–Al_2O_3	230 cc. feed per cc. catalyst per hour	450
Butene-1 Butene-2	(15.2%) (83.8%)	Activated SiO_2–Al_2O_3	230 cc. feed per cc. catalyst per hour	500
Butene-1 Butene-2	(15.2%) (83.8%)	Activated SiO_2–Al_2O_3	225 cc. feed per cc. catalyst per hour	550
Butene-1 Butene-2	(15.2%) (83.8%)	Activated SiO_2–Al_2O_3	205 cc. feed per cc. catalyst per hour	600
Butene-1 Butene-2	(15.2%) (83.8%)	Activated SiO_2–Al_2O_3	1160 cc. feed per cc. catalyst per hour	600

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene) Isomers		Other Products		References
	Butene-1	(8.7%)	*trans*-Butene-2	(34.0%)	(264)
			cis-Butene-2	(7.6%)	
1	Butene-1	(6.6%)	*trans*-Butene-2	(11.8%)	(285)
	trans-Butene-2	(6.0%)	*cis*-Butene-2	(87.4%)	
	$\frac{\text{Butene-2}}{\text{Butene-1}} = 32.33$		*n*-Butane		(600a)
	"Equilibrium conditions"				
1	Isobutene	(8.0%)	C_3H_6	(2.3%)	(158)
			C_3H_8	(0.5%)	
			C_4H_6+*n*-butenes	(74.2%)	
			C_4H_{10} fraction	(0.9%)	
			High-boiling fraction	(14.0%)	
1	Isobutene	(11.6%)	H_2	(0.1%)	(158)
			CH_4	(0.1%)	
			C_3H_6	(6.4%)	
			C_3H_8	(0.7%)	
			C_4H_6	(0.5%)	
			n-Butenes	(57.2%)	
			C_4H_{10}	(3.2%)	
			High-boiling fraction	(20.2%)	
1	Isobutene	(14.1%)	C_3H_6	(10.7%)	(158)
			C_3H_8	(2.4%)	
			C_4H_6	(0.2%)	
			n-Butenes	(42.3%)	
			C_4H_{10}	(6.0%)	
			High-boiling fraction	(24.3%)	
1	Isobutene	(15.9%)	C_2H_4	(0.04%)	(158)
			C_2H_6	(0.5%)	
			C_3H_6	(14.4%)	
			C_3H_8	(2.2%)	
			C_4H_6	(0.3%)	
			n-Butenes	(39.6%)	
			C_4H_{10}	(6.5%)	
			High-boiling fraction	(20.5%)	
1	Isobutene	(15.0%)	H_2	(0.2%)	(158)
			CH_4	(2.6%)	
			C_2H_4	(1.1%)	
			C_2H_6	(1.2%)	
			C_3H_6	(14.6%)	
			C_3H_8	(1.4%)	
			C_4H_6	(0.3%)	
			n-Butenes	(40.4%)	
			C_4H_{10}	(8.8%)	
			High-boiling fraction	(14.4%)	
1	Isobutene	(14.2%)	H_2	(0.9%)	(158)
			CH_4	(7.8%)	
			C_2H_4	(2.0%)	
			C_2H_6	(2.7%)	
			C_3H_6	(15.3%)	
			C_3H_8	(2.9%)	
			C_4H_6+*n*-butenes	(36.8%)	
			C_4H_{10}	(8.5%)	
			High-boiling fraction	(8.9%)	
1	Isobutene	(17.1%)	H_2	(0.04%)	(158)
			CH_4	(0.8%)	
			C_2H_4	(0.2%)	
			C_2H_6	(0.8%)	
			C_3H_6	(12.4%)	
			C_3H_8	(1.4%)	

Table 10. Isomeriza

Reactants: Alkene		Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Butene-1 and -2 (*Continued*)				
n-Butenes		Al_2O_3 Steam	116 sec.	294
n-Butenes		Aluminum sulfate Steam	137 sec.	294
n-Butenes		Glukhov clay Steam	138 sec.	294
n-Butenes		"Floridin" Steam	134 sec.	294
n-Butenes Isobutene *n*-Butane	(50.9%) (16.1%) (33%)	Permutite	58 sec.	400
n-Butenes Isobutene *n*-Butane	(31.2%) (28.8%) (40%)	Permutite	59 sec.	400
n-Butenes Isobutene *n*-Butane	(31.2%) (28.8%) (40%)	Permutite	170 sec.	400
n-Butenes *n*-Butane	(50%) (50%)	Sodium permutite	183 sec.	450
n-Butenes *n*-Butane	(50%) (50%)	Sodium permutite	183 sec.	450
n-Butenes		76.2% H_3PO_4+23.8% charcoal (applied at 300°) Steam	130 sec.	294
n-Butenes		33.3% H_3PO_4+67.7% charcoal (applied at 450°) Steam	122 sec.	294
n-Butenes		H_3PO_4 + silicate (dried 18–20 hours at 280–300°) Steam	120 sec.	294
n-Butenes		H_3PO_4 + silicate (dried 2–3 hours at 280–300°) Steam	144 sec.	294
n-Butenes		H_3PO_4 + silicate (dried 2–3 hours at 280–300°) Steam	280 sec.	294
n-Butenes		H_3PO_4 + silicate (dried 2–3 hours at 280–300°) Steam	288 sec.	294
n-Butenes		H_3PO_4 on kieselguhr Steam (equimolar with butenes)	10 sec.	325
n-Butenes		H_3PO_4 on kieselguhr Steam (equimolar with butenes)	40 vols. feed per vol. catalyst per hour	325
Butene-1 and/or Butene-2		H_3PO_3, HPO_3, H_3PO_4, or $H_4P_2O_7$ on carbon, silica gel, diatomaceous earth, or kieselguhr;		250–550 (325 optimum)

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene): Isomers	Products (Per cent by weight on original alkene): Other Products	References
		C_4H_6 (0.8%) n-Butenes (50.7%) C_4H_{10} (3.0%) High-boiling fraction (12.7%)	
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.00847$	Other gases Polymers (18%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.120$	C_2H_4 Other gases Polymers (15%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.0810$	C_2H_4 Other gases Polymers (37%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.0655$	C_2H_4 Other gases Polymers (34%)	(199) (200)
	Isobutene (17.1%) $\frac{\text{Isobutene}}{n\text{-Butenes}}=0.351$	n-Butenes (48.9%) n-Butane (33%?) Polymers (1%?)	(529a)
	n-Butenes (31.4%) $\frac{\text{Isobutene}}{n\text{-Butenes}}=0.818$	Isobutene (25.6%) n-Butane (40%?) Polymers (3%?)	(529a)
	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.725$	n-Butenes (29.6%) Isobutene (21.4%) n-Butane (40%?) Polymers (9%?)	(529a)
1	Isobutene (33% by vol. of exit-gas alkenes)		(257a) (421a)
	Isobutene		(417a)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.212$	C_2H_4 Other gases Polymers (2%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.531$	Other gases (large %) Polymers (43%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.173$	C_2H_4 Other gases Polymers (2%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.895$	C_2H_4 Other gases Polymers (36%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.652$	C_2H_4 Other gases Polymers (21%)	(199) (200)
1	$\frac{\text{Isobutene}}{n\text{-Butenes}}=0.420$	C_2H_4 Other gases Polymers (7%)	(199) (200)
1	Isobutene (33%)	n-Butenes (67%) Liquid (trace)	(417)
1	Isobutene (33% by vol. of exit-gas)	n-Butenes (67% by vol. of exit-gas) Liquid (trace)	(420)
1–10	Isobutene	Isooctenes	(417)

Table 10. Isomeriza

Reactants: Alkene		Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Butene-1 and/or -2 (*Continued*)		Added phosphotungstic or phosphomolybdic acids if desired; Steam		
n-Butenes		H_3PO_4 on kieselguhr	50 sec.	325
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)	80.0 sec.	275
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)	10.0 sec.	275
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)	5.40 sec.	275
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 275° in vacuo before use)	3.70 sec.	275
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)	43.6 sec.	325
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)	10.8 sec.	325
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)	5.00 sec.	325
n-Butenes *n*-Butane	(51.4%) (48.6%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) (heated at 325° in vacuo before use)	2.05 sec.	325
n-Butenes Isobutene	(97%) (3%)	82% H_3PO_4 (conc. about 89%) +18% kieselguhr (dried at 250°) Steam (equimolar with butenes)	29.9–31.7 sec. 27.6 sec. 26.8–28.2 sec. 10.2–25.3 sec.	225 250 275 325
n-Butenes Isobutene	(96–98%) (2–4%)	H_3PO_4 on chamotte (dried at 200–400°)		200–400
Butene-1 *cis*-Butene-2 *trans*-Butene-2 Isobutene	(12.3%) (13.2%) (20.0%) (54.5%)	H_3PO_4 on chamotte Steam	312 sec.	225
Butene-1 *cis*-Butene-2 *trans*-Butene-2 Isobutene	(14.0%) (15.0%) (22.8%) (48.2%)	H_3PO_4 on chamotte Steam	219 sec.	294
Butene-1 *cis*-Butene-2 *trans*-Butene-2	(27.0%) (29.0%) (44.0%)	H_3PO_4 on chamotte Steam	224 sec.	294
Butene-1 *cis*-Butene-2 *trans*-Butene-2 Isobutene	(0.70%) (0.75%) (1.14%) (97.4%)	H_3PO_4 on chamotte Steam	210 sec.	294
Butene-1 *cis*-Butene-2 *trans*-Butene-2	(27.0%) (29.0%) (44.0%)	H_3PO_4 on chamotte Steam	262 sec.	355

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene) Isomers		Other Products		References
1	Isobutene Isobutene	(9.2%)	Alkenes (gaseous) Polymers	(113%)	(421) (609a)
1	Isobutene	(24.3%)	Alkenes (gaseous) Polymers	(58%)	(609a)
1	Isobutene	(25.3%)	Alkenes (gaseous) Polymers	(41%)	(609a)
1	Isobutene	(23.3%)	Alkenes (gaseous) Polymers	(23%)	(609a)
1	Isobutene	(16.2%)	Alkenes (gaseous) Polymers	(42%)	(609a)
1	Isobutene	(30.2%)	Alkenes (gaseous) Polymers	(30%)	(609a)
1	Isobutene	(32.1%)	Alkenes (gaseous) Polymers	(16%)	(609a)
1	Isobutene	(15.6%)	Alkenes (gaseous)		(609a)
1 1 1 1	$\frac{\text{Isobutene}}{n\text{-Butenes}}$ = 0.088–0.069 0.075 0.676–0.413 0.511–0.695				(609a)
1	Isobutene	(15–40%)	*n*-Butenes Polymers		(200)
1			*n*-Butenes Isobutene Polymers	(15.0%) (14.0%) (67.0%)	(540)
1			*n*-Butenes Isobutene Polymers	(47.4%) (45.6%) (7.0%)	(540)
1	Isobutene	(17.4%)	*n*-Butenes Polymers	(61.6%) (21.0%)	(540)
1	*n*-Butenes	(23.5%)	Isobutene Polymers	(45.5%) (31.0%)	(540)
1	Isobutene	(28.6%)	*n*-Butenes Polymers	(54.4%) (17.0%)	(540)

Table 10. Isomeriza

Reactants: Alkene	Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Butene-1 (0.70%) *cis*-Butene-2 (0.75%) *trans*-Butene-2 (1.14%) Isobutene (97.4%)	H_3PO_4 on chamotte Steam	311 sec.	355
Butene-1 (10.8%) *cis*-Butene-2 (11.6%) *trans*-Butene-2 (17.6%) Isobutene (60.0%)	H_3PO_4 on chamotte Steam	317 sec.	355
"Isomerization is effected between isobutene and its normal isomers"	Zeolite	120–250 sec.	400–500
Isobutene	H_3PO_4 on chamotte (dried at 200–400°) Steam, N_2, or CO_2 (as diluent to reduce polymerization)		200–400
Isobutene	H_3PO_4+silicate (dried 2–3 hours at 280–300°) Steam	210 sec.	294
Isobutene	H_3PO_4+silicate (dried 2–3 hours at 280–300°) Steam	246 sec.	294
Pentene-1		8–22 sec.	550–600
Pentene-1	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	357
Pentene-1	Activated SiO_2–Al_2O_3	150 g. feed per 100 cc. catalyst per 0.75 hour	400
Pentene-1	100 SiO_2 + 5Al_2O_3 + 0.5 ThO_2 (prepared by dehydrating the mixed hydrates at 482°)	3 cc. liquid feed per cc. catalyst per hour	399
Pentene-2		8–22 sec.	550–600
Pentene-2	Xylene (solvent)	8 or 16	100
Pentene-2	Irradiated by Mazda lamp Xylene (solvent)	8	50–60
Pentene-2	Irradiated by Mazda lamp	8	80–90
Pentene-2	Irradiated by Mazda lamp Xylene (solvent)	8	90–100
Pentene-2	Irradiated by Mazda lamp Xylene (solvent)	14.5	145–160

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene) Isomers		Other Products		References
1	n-Butenes	(34.7%)	Isobutene Polymers	(38.3%) (27.0%)	(540)
1	n-Butenes	(44.0%)	Isobutene Polymers	(40.0%) (16.0%)	(540)
vapor phase	See Canadian Patent 388,423 for further details				(257)
1	n-Butenes	(up to 40%)	Polymers	(4%)	(200)
1	n-Butenes	(23.5%)	Isobutene Polymers	(45.5%) (31%)	(199) (200)
1	n-Butenes	(43.3%)	Isobutene Polymers	(26.7%) (30%)	(199) (200)
1	Pentene-2		Pentene-1		(261) (265)
slightly above 1	Pentene-2	(78.3%)	Pentene-1	(21.7%)	(172a)
1	2-Methylbutenes	(59.0%)	H_2 CH_4, C_2H_6, C_3H_8 fraction C_2H_4 Propene+n-butenes Isobutene C_4H_{10} fraction C_5 fraction (additional) C_6 fraction C_7–C_9 fraction C_{10}–C_x fraction	(0.01%) (0.5%) (0.1%) (3.0%) (3.0%) (1.0%) (12.7%) (7.7%) (3.8%) (5.1%)	(158)
1	2-Methylbutenes	(59%)	Gas C_5 fraction (additional) Higher fractions	(7%) (13%) (17%)	(581a)
1	Pentene-1		Pentene-2		(261) (265)
	Shown by HBr product composition: 2-bromopentane 3-bromopentane	 (32%) (68%)			(302)
	No change shown by HBr product composition: 2-bromopentane 3-bromopentane	 (22%) (78%)			(302)
	Shown by HBr product composition: 2-bromopentane 3-bromopentane	 (29%) (71%)			(302)
	Shown by HBr product composition: 2-bromopentane 3-bromopentane	 (32%) (68%)			(302)
	Shown by HBr product composition: 2-bromopentane 3-bromopentane	 (29%) (71%)			(302)

Table 10. Isomeriza

Reactants: Alkene	Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Pentene-2	Ultraviolet light	6	
Pentene-2	Ultraviolet light	8	
Pentene-2	Ultraviolet light	16	
Pentene-2	Ultraviolet light	29	
Pentene-2	Ultraviolet light Later, "aging"	29 (irradiation) 2 days ("aging")	
Pentene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	2.5 passes in 3 hours	266
Pentene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	299
Pentene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	5 passes in 6 hours	300
Pentene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	2.5 passes in 3 hours	358
Pentene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	5 passes in 6 hours	359
Pentene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	358
Pentene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	15 passes in 18 hours	364
Pentene-2	75% Al_2O_3+25% CoO	10 passes in 12 hours	320
Pentene-2	75% Al_2O_3+25% CoO	10 passes in 12 hours	375
Pentene-2	75% Al_2O_3+25% Cr_2O_3	10 passes in 12 hours	295
Pentene-2	75% Al_2O_3+25% Cr_2O_3	10 passes in 12 hours	345
Pentene-2	50% Al_2O_3+50% Fe_2O_3	10 passes in 12 hours	295
Pentene-2	50% Al_2O_3+50% Fe_2O_3	10 passes in 12 hours	344
Pentene-2	75% Al_2O_3+25% MnO	10 passes in 12 hours	301
Pentene-2	75% Al_2O_3+25% MnO	10 passes in 12 hours	305
Pentene-2	75% Al_2O_3+25% MnO	10 passes in 12 hours	362
Pentene-2	75% Al_2O_3+25% MnO	10 passes in 12 hours	366
cis-Pentene-2 *cis*-Pentene-2	Xylene (solvent) Heated (65 hours) Sunlight (13 weeks) (consecutively)	(?) 65 13 weeks	90–100 at 70–80 at room
cis-Pentene-2 *cis*-Pentene-2	Ultraviolet light Ultraviolet light	4.5 8.5	b.p. (?) b.p. (?)

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene) Isomers		Other Products		References
	Shown by HBr product composition: 2-bromopentane	(30%)			(302)
	3-bromopentane	(70%)			
	Shown by HBr product composition: 2-bromopentane	(38%)			(302)
	3-bromopentane	(62%)			
	Shown by HBr product composition: 2-bromopentane	(42%)			(302)
	3-bromopentane	(58%)			
	Shown by HBr product composition: 2-bromopentane	(49%)			(302)
	3-bromopentane	(51%)			
	Shown by HBr product composition: 2-bromopentane	(38%)			(302)
	3-bromopentane	(62%)			
slightly above 1	Pentene-1	(1.9%)	Pentene-2	(98.1%)	(172a)
slightly above 1	Pentene-1	(9.3%)	Pentene-2	(90.7%)	(172a)
slightly above 1	Pentene-1	(8.0%)	Pentene-2	(92.0%)	(172a)
slightly above 1	Pentene-1	(9.9%)	Pentene-2	(90.1%)	(172a)
slightly above 1	Pentene-1	(14.4%)	Pentene-2	(85.6%)	(172a)
slightly above 1	Pentene-1	(15.7%)	Pentene-2	(84.3%)	(172a)
slightly above 1	Pentene-1	(15.2%)	Pentene-2	(84.8%)	(172a)
slightly above 1	Pentene-1	(4.6%)	Pentene-2	(95.4%)	(172a)
slightly above 1	Pentene-1	(13.5%)	Pentene-2	(86.5%)	(172a)
slightly above 1	Pentene-1	(11.7%)	Pentene-2	(88.3%)	(172a)
slightly above 1	Pentene-1	(13.3%)	Pentene-2	(86.7%)	(172a)
slightly above 1	Pentene-1	(6.8%)	Pentene-2	(93.2%)	(172a)
slightly above 1	Pentene-1	(10.5%)	Pentene-2	(89.5%)	(172a)
slightly above 1	Pentene-1	(9.3%)	Pentene-2	(90.7%)	(172a)
slightly above 1	Pentene-1	(10.6%)	Pentene-2	(89.4%)	(172a)
slightly above 1	Pentene-1	(15.3%)	Pentene-2	(84.7%)	(172a)
slightly above 1	Pentene-1	(15.4%)	Pentene-2	(84.6%)	(172a)
sealed tube	*trans*-Pentene-2				(301)
sealed tube	*trans*-Pentene-2				(545)
1	*trans*-Pentene-2		*cis*-Pentene-2		(545)
1	*trans*-Pentene-2		*cis*-Pentene-2		(545)

Table 10. Isomeriza

Reactants: Alkene	Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
cis-Pentene-2	$CH_3 . CO_2H$ (catalyst)	(?)	room
trans-Pentene-2	Ultraviolet light	8.5	b.p. (?)
trans-Pentene-2	$CH_3 . CO_2H$ (catalyst)	(?)	room
n-Pentenes	Al_2O_3 (calcined)		450
n-Pentenes	Sodium permutite	33 sec.	400
n-Pentenes	Sodium permutite	33 sec.	400
n-Pentenes	Sodium permutite	62 sec.	450
n-Pentenes	Sodium permutite	62 sec.	450
"Amylenes" insoluble as vapors in 68% H_2SO_4	Mixture of metaphosphoric and pyrophosphoric acids on diatomaceous earth		200–350
2-Methylbutene-1	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	357
3-Methylbutene-1	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	20 passes in 24 hours	362
3-Methylbutene-1	Al_2O_3	16 sec.	450
3-Methylbutene-1	Al_2O_3 in Cu or glass tubes		450
3-Methylbutene-1	Al_2O_3 in Cu tube	40 g. feed per 2 hours	525–535
2-Methylbutene-1 } 3-Methylbutene-1 }	Al_2O_3 in Cu tube	77 g. feed per 40 min.	540–560
3-Methylbutene-1	Siliceous earth in Cu tube		500–505
3-Methylbutene-1	Glass tube		400
3-Methylbutene-1	Glass tube		500
3-Methylbutene-1	Glass tube	25 g. feed per hour	530, 540, or 550
3-Methylbutene-1	Glass tube	38 g. feed per 35 min.	600
3-Methylbutene-1	Aluminum sulfate ("A sample of commercial alum was heated in an iron dish until the water of crystallization was just driven off.")	16 sec.	425
3-Methylbutene-1	H_3PO_4 on pumice	14 sec.	500
3-Methylbutene-1	H_2SO_4 (conc. over 60%?)		30–35 (?)
3-Methylbutene-1 (?)	$AlCl_3$ (50%)	5 weeks	0–20
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	20 passes in 24 hours	251
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	2.5 passes in 3 hours	263
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	266
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	2.5 passes in 3 hours	300
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	300
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	2.5 passes in 3 hours	355
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	5 passes in 6 hours	354
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	356
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	15 passes in 18 hours	356
2-Methylbutene-2	Activated Al_2O_3 (Grade A, 8–14 mesh, Aluminum Ore Co.)	10 passes in 12 hours	400

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene): Isomers		Other Products		References
1	*trans*-Pentene-2	(small %)	*cis*-Pentene-2		(98)
1	*cis*-Pentene-2	(small %)	*trans*-Pentene-2		(544)
1	*cis*-Pentene-2	(small %)	*trans*-Pentene-2		(98)
	3-Methylbutene-1 2-Methylbutene-2	(small %)	*n*-Pentenes		(33)
1 (?)	2-Methylbutenes	(about 45%)	Undescribed	(about 55%)	(421a)
1 (?)	2-Methylbutenes (about 53% by vol. of exit-gas)				(257a)
1 (?)	2-Methylbutenes	(about 47%)	Undescribed	(about 53%)	(421a)
1 (?)	2-Methylbutenes (about 56% by vol. of exit-gas)				(257a)
1	"Amylenes" soluble 50% as vapors in 68% H_2SO_4				(200)
slightly above 1	3-Methylbutene-1 2-Methylbutene-2	(3.6%) (69.4%)	2-Methylbutene-1	(27.0%)	(172a)
slightly above 1	2-Methylbutene-1 2-Methylbutene-2	(27.6%) (68.6%)	3-Methylbutene-1	(3.8%)	(172a)
	2-Methylbutene-2	(10%)	3-Methylbutene-1		(413)
	2-Methylbutene-2	(55%)	3-Methylbutene-1	(37%)	(271)
	2-Methylbutene-2	(66%)	Gas		(271)
	2-Methylbutene-2	(below 80%)			(271)
	2-Methylbutene-2				(271)
	2-Methylbutene-2	(trace)			(271)
	2-Methylbutene-2	(trace)			(271)
	2-Methylbutene-2	(small %)			(271)
	2-Methylbutene-2	(trace)	Gases		(271)
	2-Methylbutene-2	(47%)			(413)
	2-Methylbutene-2	(29%)			(413)
1	2-Methylbutene-2	(small %)			(413)
1	Methylcyclobutane		Cyclanes resembling lubricating oil A hexane		(16)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(22.6%) (1.8%)	2-Methylbutene-2	(75.6%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(17.3%) (0.0%)	2-Methylbutene-2	(82.7%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(22.2%) (0.6%)	2-Methylbutene-2	(77.2%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(20.0%) (0.6%)	2-Methylbutene-2	(79.4%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(25.6%) (2.5%)	2-Methylbutene-2	(71.9%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(20.9%) (1.1%)	2-Methylbutene-2	(78.0%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(27.7%) (1.8%)	2-Methylbutene-2	(70.4%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(27.3%) (3.1%)	2-Methylbutene-2	(69.6%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(26.9%) (3.7%)	2-Methylbutene-2	(69.4%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(28.2%) (5.0%)	2-Methylbutene-2	(66.8%)	(172a)

Table 10. Isomeriza

Reactants: Alkene		Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
2-Methylbutene-2		Al_2O_3		520–530 or 540–550
2-Methylbutene-2		75% Al_2O_3+25% CoO	10 passes in 12 hours	311
2-Methylbutene-2		75% Al_2O_3+25% CoO	10 passes in 12 hours	370
2-Methylbutene-2		75% Al_2O_3+25% Cr_2O_3	10 passes in 12 hours	294
2-Methylbutene-2		75% Al_2O_3+25% Cr_2O_3	10 passes in 12 hours	345
2-Methylbutene-2		50% Al_2O_3+50% Fe_2O_3	10 passes in 12 hours	296
2-Methylbutene-2		50% Al_2O_3+50% Fe_2O_3	10 passes in 12 hours	347
2-Methylbutene-2		75% Al_2O_3+25% MnO	10 passes in 12 hours	300
2-Methylbutene-2		75% Al_2O_3+25% MnO	10 passes in 12 hours	310
2-Methylbutene-2		75% Al_2O_3+25% MnO	10 passes in 12 hours	361
2-Methylbutene-2		75% Al_2O_3+25% MnO	10 passes in 12 hours	363
2-Methylbutene-2		Permutite	33 sec.	400
2-Methylbutene-2 *n*-Pentenes	(80%) (20%)	Permutite	33 sec.	400
2-Methylbutene-2 *n*-Pentenes	(60%) (40%)	Permutite	33 sec.	400
Hexene-1		Al_2O_3 Sample A	3.1 cc. feed per 10 g. catalyst per hour	398
Hexene-1		Al_2O_3 Sample B	3.1 cc. feed per 10 g. catalyst per hour	398
Hexene-1		Al_2O_3	11.2 cc. feed per 10 g. catalyst per hour	398
Hexene-1		Al_2O_3	22.5 cc. feed per 10 g. catalyst per hour	398

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene) Isomers		Other Products		References
"constant"	No isomers				(271)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(11.1%) (1.2%)	2-Methylbutene-2	(87.7%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(25.8%) (6.1%)	2-Methylbutene-2	(68.1%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(25.1%) (2.5%)	2-Methylbutene-2	(72.4%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(26.6%) (5.2%)	2-Methylbutene-2	(68.2%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(26.2%) (1.3%)	2-Methylbutene-2	(72.5%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(28.5%) (3.3%)	2-Methylbutene-2	(68.2%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(21.1%) (1.8%)	2-Methylbutene-2	(77.1%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(21.1%) (1.2%)	2-Methylbutene-2	(77.7%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(25.9%) (4.1%)	2-Methylbutene-2	(70.0%)	(172a)
slightly above 1	2-Methylbutene-1 3-Methylbutene-1	(26.5%) (4.3%)	2-Methylbutene-2	(69.2%)	(172a)
1	*n*-Pentenes $\frac{\text{2-Methylbutenes}}{n\text{-Pentenes}} = 3.48$	(19%)	2-Methylbutenes Side products	(66%) (15%)	(529a)
1	$\frac{\text{2-Methylbutenes}}{n\text{-Pentenes}} = 4.56$		*n*-Pentenes 2-Methylbutenes Side products	(16%) (73%) (11%)	(529a)
1	$\frac{\text{2-Methylbutenes}}{n\text{-Pentenes}} = 2.08$		*n*-Pentenes 2-Methylbutenes Side products	(28%) (58%) (14%)	(529a)
1	Hexene-3 2-Methylpentene-2 Lower-boiling 3-methylpentene-2 Higher-boiling 3-methylpentene-2 2-Ethylbutene-1	(11.3%) (27.7%) (9.8%) (5.3%) (38.7%)	Hexene-1 Carbon on catalyst	(5.9%)	(220)
1	Hexene-3 2-Methylpentene-2 Lower-boiling 3-methylpentene-2 Higher-boiling 3-methylpentene-2 2-Ethylbutene-1	(10.6%) (27.9%) (10.2%) (5.2%) (38.3%)	Hexene-1 Carbon on catalyst	(6.3%)	(220)
1	Hexene-2 Hexene-3 2-Methylpentene-2 Lower-boiling 3-methylpentene-2 Higher-boiling 3-methylpentene-2 2-Ethylbutene-1	(2%) (8%) (12%) (36%) (5%) (13%)	Hexene-1	(24%)	(220)
1	Lower-boiling 3-methylpentene-2 2-Ethylbutene-1	(9.2%) (1.8%)	Hexene-1	(89%)	(220)

Table 10. Isomeriza

Reactants: Alkene	Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Hexene-1	Al_2O_3	45.5 cc. feed per 10 g. catalyst per hour	398
Hexene-1	ThO_2	3.12 cc. feed per 10 g. catalyst per hour	398
Hexene-1	MoS_3 (5%)	1	400
Hexene-1	$ZnCl_2$ on pumice (1 : 1) (total 69%)	1.5	300–325
Hexene-1	H_3PO_4 on pumice (1 : 1) (55.6%)	4–5	325–350
n-Hexenes	Al_2O_3 (calcined)		400
2-Methylpentene-2	Al_2O_3	3.12 cc. feed per 10 g. catalyst per hour	398
2-Methylpentene-2	ThO_2	3.12 cc. feed per 10 g. catalyst per hour	398
Lower-boiling 3-methylpentene-2	Al_2O_3	3.12 cc. feed per 10 g. catalyst per hour	398
Lower-boiling 3-methylpentene-2	Al_2O_3	3.12 cc. feed per 10 g. catalyst per hour	440
Lower-boiling 3-methylpentene-2	ThO_2	3.12 cc. feed per 10 g. catalyst per hour	398
Lower-boiling 3-methylpentene-2	ThO_2	3.12 cc. feed per 10 g. catalyst per hour	440
2-Ethylbutene-1	ThO_2	3.12 cc. feed per 10 g. catalyst per hour	398
3,3-Dimethylbutene	P_2O_5 on silica gel		300
3,3-Dimethylbutene	Activated Al_2O_3	20 cc. feed per hour	350
3,3-Dimethylbutene	$Al_2(SO_4)_3$	30 cc. feed per hour	275
3,3-Dimethylbutene (large %) 2,3-Dimethylbutenes (small %)	$Al_2(SO_4)_3$		280–290
3,3-Dimethylbutene	Sodium permutite	30 sec.	310
3,3-Dimethylbutene	Permutite or phosphoric acid type of catalysts	short	310

ion of Alkenes—Continued

Products	Refer-
Other Products	ence
(per cent by weight on original olefine)	
Lower-boiling 3-methyl- pentene-2 (8%)	(220)
Lower-boiling 3-methyl- pentene-2 (90%); Polymers (5%); 2-Ethylbutene-1	(220)
Hexene-2; Polymers	(437)
Isohexones; High-boiling products	(436)
2-Methylpentene-2 (15%)	(438)
3-Methylpentene-2 and/or 2-Ethylbutene-1	(33)
Lower-boiling 3-methyl- pentene-2 (35%); 2-Methylpentene-2; Polymers	(220)
Lower-boiling 3-methyl- pentene-2 (70%); 2-Methylpentene-2 (3%); Polymers; 2-Ethylbutene-1 (25%)	(220)
3-methyl- 2-Methylpentene-2; 2-Ethylbutene-1; Lower-boiling pentene-2; Polymers	(220)
3-methyl- 2-Methylpentene-1; 2-Methylpentene-2; 2-Ethylbutene-1; Lower-boiling pentene-2; Isohexane; Polymers	(220)
3-methyl- 2-Methylpentene-2; 2-Ethylbutene-1; Lower-boiling pentene-2; Polymers	(220)
3-methyl- 2-Methylpentene-1; 2-Methylpentene-2; 2-Ethylbutene-1; Lower-boiling pentene-2; Isohexane; Polymers	(220)
2-Methylpentene-2 (3%); 2-Methylbutene-1; Polymers; Lower-boiling 3-methyl- pentene-2 (69%)	(220)
(trace) Dimethylbutene	(220)

Table 10. Isomeriza

Reactants: Alkene		Reactants: Catalyst (Per cent by weight on alkene+catalyst)		Contact Time (hours)	Temp. (°C.)
2,3-Dimethylbutene-1		P_2O_5 on silica gel			300
2,3-Dimethylbutene-2		P_2O_5 on silica gel			300
Heptene-1		Al_2O_3		3.12 cc. feed per 10 g. catalyst per hour	398
Heptene-1		BeO		5 g. feed per ? 44.2 cc. of catalyst per hour (retreated the b.p. 92–95° fraction from the initial product)	450
2-Methylhexene-2		Al_2O_3		3.12 cc. feed per 10 g. catalyst per hour	398
2-Methylhexene-2		ThO_2		3.12 cc. feed per 10 g. catalyst per hour	398
3-Methylhexene-2		Al_2O_3		3.12 cc. feed per 10 g. catalyst per hour	398
3-Methylhexene-2		Al_2O_3		3.12 cc. feed per 10 g. catalyst per hour	440
3-Methylhexene-2		ThO_2		3.12 cc. feed per 10 g. catalyst per hour	398
3-Methylhexenc-2		ThO_2		3.12 cc. feed per 10 g. catalyst per hour	440
2-Ethylpentene-1		ThO_2		3.12 cc. feed per 10 g. catalyst per hour	398
Octene-1 } Octene-2 }		Quartz tube			295–365
Octene-1 } Octene-2 }	(91.7%)	Glass tube used		836 min.	345
Isooctenes	(8.3%)				
Octene-1 } Octene-2 }	(91.7%)	Glass tube used		1.50	380
Isooctenes	(8.3%)				
Octene-1 } Octene-2 }	(91.7%)	Glass tube used		2.95	380
Isooctenes	(8.3%)				
Octene-1 } Octene-2 }	(91.7%)	Glass tube used		5.75	380
Isooctenes	(8.3%)				
Octene-1 } Octene-2 }		$ZnCl_2$	(21.7%)	1.5	300–325

...tion of Alkenes—*Continued*

	Products	Refs.
	by weight on original olefin; Pressure Other Products	
(15%) 3-Methylbutene-1	2,3-Dimethylbutene-1; 2,3-Dimethylbutene-2 (60%); 2,3-Dimethylbutene-1 (15%); 3-Methylhexene-1 (70%); 2-Ethylpentene-1 (5%)	(220)
(below 60%)	3-Methylhexene-1 (below 60%)	(13a)
(48%) Methylhexene-1	3-Methylhexene-2 (40%); 2-Ethylpentene-1 (1%); Polymers	(220)
(3%) Methylhexene-1	3-Methylhexene-2 (70%); 2-Ethylpentene-1 (20%); Polymers	(220)
(83%) Methylhexene-2	3-Methylhexene-1 (10%); 2-Ethylpentene-1 (8%); Polymers	(220)
(63%) Methylhexene-1	3-Methylhexene-2 (18%); 2-Methylhexene-2 (5%); Isoheptene; 2-Ethylpentene-1 (3%); Polymers	(220)
(76%) Methylhexene-1	3-Methylhexene-2 (3%); 2-Ethylpentene-1 (1%); Polymers	(220)
(45%) Methylhexene-1	3-Methylhexene-2 (11%); 2-Methylhexene-2 (8%); Isoheptene; 2-Ethylpentene-1 (20%); Polymers	(220)
(21%) Ethylpentene-1	2-Methylhexene-1 (3%); 3-Methylhexene-2 (7%); Polymers	(220)
(1%) Isooctenes		(259)

Table 10. Isomeriza

Reactants: Alkene	Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Octene-1, Octene-2	$ZnCl_2$ on pumice (1 : 1) (total 45.5%)	25	325–350
Octene-1, Octene-2	$ZnCl_2$ on pumice (1 : 1) (total 45.5%) Steam	25	325–350
Octene-1, Octene-2	$ZnCl_2$ on pumice (1 : 1) (total 73.5%)	13	325–350
Octene-1, Octene-2	Reused-$ZnCl_2$ on pumice (1 : 1) (total 73.5%)	13	325–350
Octene-1, Octene-2	$ZnCl_2$ on pumice (1 : 1) (total 70.8%)	0.50	300–325
Octene-1, Octene-2	$ZnCl_2$ on pumice (1 : 1) (total 70.8%)	1	300–325
Octene-1, Octene-2	$ZnCl_2$ on pumice (1 : 1) (total 67.6%)	1.5	300–325
Octene-1, Octene-2	$ZnCl_2$ on pumice (1 : 1) (total 70.8%)	1.5	300–325
Octene-1, Octene-2	H_3PO_4 on pumice (1 : 1) (total 65.2%)	1.5	400
Octene-1, Octene-2	Activated SiO_2-Al_2O_3	720 g. feed per per 100 cc. catalyst per 2.45 hours	375
Octene-1, Octene-2	Activated SiO_2-Al_2O_3	151 g. feed per per 100 cc. catalyst per 0.5 hour	385
Octene-1, Octene-2	100 SiO_2+5 Al_2O_3+0.5 ThO_2 (prepared by dehydrating the mixed hydrates at 482°)	4 cc. liquid feed per cc. catalyst per hour	385
n-Octenes	Sodium permutite	60 sec.	300
n-Octenes	Sodium permutite	60 sec.	300
2,4,4-Trimethylpentenes-1 and -2	H_3PO_4		
3,7-Dimethyloctene-1	Pd-asbestos	long	200
Hexadecene	Activated SiO_2-Al_2O_3	1230 g. feed per 100 cc. catalyst per 3.93 hours	300
Hexadecene	Activated SiO_2-Al_2O_3	1255 g. feed per 100 cc. catalyst per 4.0 hours	350

...tion of Alkenes—*Continued*

Products (per cent by weight on original material)	Pressure (atmos)	Other Products	Ref.
Isododecenes (12%)	1		(436)
Isododecenes (18.3%)	1		(436)
Isododecenes (25%)	1		(436)
Isododecenes (17%)	1		(436)
Isododecenes (22%)	50 (N_2)	Low-boiling product	(436)
Isododecenes (23%)	50 (N_2)	Low-boiling product	(436)
Isododecenes	50 (N_2)	(14%) Fraction, b.p. 80–100°; (10%) Fraction, b.p. 130–200°; (15%) Fraction, b.p. 200–230°	(436)
Isododecenes (14%)	50 (N_2)	Low-boiling product	(436)
Isododecenes (17%)	50 (N_2)	Low-boiling product	(436)
Isododecenes (58.3%)	1	(0.0003%) ...; (0.4%); (2.5%); (6.4%); (2.3%) n-Butenes; (3.0%) Isobutene; (0.8%) C_5 fraction; (10.9%) C_6+C_7 fraction; (20.6%) Octenes	(158)
Isododecenes (60.5%)	1	(6.2%); (6.2%); (5.9%) n-Butenes; (6.9%) Isobutene; (0.9%) C_5 fraction; (8.3%) C_6+C_7 fraction; (14.0%) Octenes	(158)
Isododecenes (61%)		(11%) Isooctenes; gas; (8%) Octenes-1 and -2	(581a)
Methyl... (68%)		(15%) ...; p-Octenes	(257a), (421a)
Isooctenes (See British Patent 501,896 for further details)			(417a)
A 2,3,4-Trimethylpentene			(551a)
Dimethyloctene-2 (100%)			(670)

Table 10. Isomeriza

Reactants: Alkene	Reactants: Catalyst (Per cent by weight on alkene+catalyst)	Contact Time (hours)	Temp. (°C.)
Hexadecene (*Continued*)			
Hexadecene	Activated SiO_2-Al_2O_3	1270 g. feed per 100 cc. catalyst per 4.0 hours	400
Hexadecene	Activated SiO_2-Al_2O_3	885 g. feed per 100 cc. catalyst per 2.78 hours	450
Alkenes	H_3PO_4 or neutral sulfates or phosphates of metals of the first, second, or third group or of Fe, Co, Ni, Cr, or Mn on a carrier		200–400
Alkenes	Hydrated aluminum silicate having base-change properties		275–500

tion of Alkenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkene) Isomers		Other Products		References
			C_5–C_{15} fraction	(5.7%)	
			Hexadecene and heavier	(47.5%)	
1	Isohexadecenes	(26.9%)	C_2H_4	(0.1%)	(158)
			C_2H_6	(0.02%)	
			C_3H_6	(1.0%)	
			C_3H_8	(0.08%)	
			n-Butenes	(1.4%)	
			Isobutene	(1.4%)	
			C_4H_{10} fraction	(0.5%)	
			C_5–C_{15} fraction	(48.8%)	
			Hexadecene and heavier	(18.3%)	
1	Isohexadecenes	(13.0%)	C_3H_6	(3.8%)	(158)
			C_3H_8	(0.4%)	
			n-Butenes	(4.6%)	
			Isobutene	(4.2%)	
			C_4H_{10} fraction	(1.1%)	
			C_5–C_{15} fraction	(67.5%)	
			Hexadecene and heavier	(1.1%)	
	Isomers				(200)
	Isomers				(257)

Table 11. Isomerization

Reactants: Allenic Alkadiene	Reactants: Catalyst (Per cent by weight on alkadiene+catalyst)	Contact Time (hours)	Temp. (°C.)
Propadiene	Na (9%) Ether (solvent) (83%)	24	100
Propadiene	"Floridin"	10.0 cc. feed per 26.5 cc. catalyst per min.	167
Propadiene	"Floridin"	12.0 cc. feed per 26.5 cc. catalyst per min.	220
Propadiene	"Floridin"	10.0 cc. feed per 26.5 cc. catalyst per min.	230
Propadiene	"Floridin"	10.1 cc. feed per 26.5 cc. catalyst per min.	250
Propadiene	"Floridin"	10.7 cc. feed per 26.5 cc. catalyst per min.	270
Propadiene	"Floridin"	8.3 cc. feed per 26.5 cc. catalyst per min.	286
Propadiene	"Floridin"	10.0 cc. feed per 26.5 cc. catalyst per min.	312
Propadiene	"Floridin"	5.0 cc. feed per 26.5 cc. catalyst per min.	325
Propadiene	"Floridin"	5.0 cc. feed per 26.5 cc. catalyst per min.	345
Propadiene	"Floridin"	8.3 cc. feed per 26.5 cc. catalyst per min.	350
Propadiene	Alcoholic potash	12	160–170
Butadiene-1,2	Na Ether (solvent)	10 (?)	heated
Butadiene-1,2	"Floridin"		245–330
Butadiene-1,2	Alcoholic potash	9	170
Pentadiene-1,2	$NaNH_2$ "Vaseline" Xylene (?) or petroleum (b.p. above 180°) (?)	2	140
3-Methylbutadiene-1,2		2–20 days	100–225

of Allenic Alkadienes

	Pressure (atms.)	Products (Per cent by weight on original alkadiene) Isomers	Other Products	References
	sealed tube	Propyne (Na derivative)		(239)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.1806$		(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.2438$	Polymers (6.25%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.3263$	Polymers (18.0%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.4493$	Polymers (20.0%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.7857$	Polymers (37.5%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.8692$	Polymers (46.0%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=1.237$	Polymers (58.3%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=1.597$	Polymers (60.0%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.5175$	Polymers (65.0%)	(552)
	1	$\frac{\text{Propyne}}{\text{Propadiene}}=0.5038$	Polymers (66.7%)	(552)
0		Propyne	Propadiene Ethyl isopropenyl ether	(179)
1		Butyne-1 (Na derivative)	Butene	(292)
30		Butyne-1 (3.4%) Butadiene-1,2 (trace)		(549)
		Butyne-2		(292)
	1	Pentyne-1 (Na derivative) (large %)	NH_3 (off at 100–120°)	(79)
225	bomb tube	2-Methylbutadiene-1,3 (small %)	1,2-Diisopropylidenecyclobutane 1,1-Dimethyl-2-methylene-3-isopropylidenecyclobutane Dipentene	(330)

Table 11. Isomerization

Reactants: Allenic Alkadiene	Reactants: Catalyst (Per cent by weight on alkadiene+catalyst)	Contact Time (hours)	Temp. (°C.)
3-Methylbutadiene-1,2	Activated "Floridin"	0.26 g. feed per min.	215
3-Methylbutadiene-1,2	Activated "Floridin"	0.23 g. feed per min.	232
3-Methylbutadiene-1,2	Activated "Floridin"	0.23 g. feed per min.	280
3-Methylbutadiene-1,2	Activated "Floridin"	0.3 g. feed per min.	334
3-Methylbutadiene-1,2	Na		100
3-Methylbutadiene-1,2	Quinoline hydrobromide (15–20% solution) Quinoline (solvent)	10–12	130–135
3-Methylbutadiene-1,2	Al metal or Al compounds		heated
3-Methylbutadiene-1,2	Al_2O_3		300
3-Methylbutadiene-1,2	Al_2O_3		300
Heptadiene-1,2	$NaNH_2$ "Vaseline" Xylene (?) or petroleum (b.p above 180°) (?)	2	140
5-Methylhexadiene-1,2	$NaNH_2$ "Vaseline" Xylene (?) or petroleum (b.p. above 180°) (?)	2	140
4,4-Dimethylpentadiene-1,2	Na		heated
4,4-Dimethylpentadiene-1,2	"Floridin"		230–235
2,4-Dimethylpentadiene-2,3		5 days	150
2,4-Dimethylpentadiene-2,3	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	120
2,4-Dimethylpentadiene-2,3 (94.9%) 2,4-Dimethylpentadiene-1,3 (5.1%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	170
2,4-Dimethylpentadiene-2,3 (93.3%) 2,4-Dimethylpentadiene-1,3 (6.7%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	202
2,4-Dimethylpentadiene-2,3	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	204
2,4-Dimethylpentadiene-2,3 (73.0%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc.	205

Allenic Alkadienes—Continued

Products

% by weight on original

Isomers | Other Products

3-Methylbutyne-1 / 3-Methylbutadiene-1,2 = 0.3463

3-Methylbutyne-1 / 3-Methylbutadiene-1,2 = 1.066

3-Methylbutyne-1 / 3-Methylbutadiene-1,2 = 1.454

3-Methylbutyne-1 / 3-Methylbutadiene-1,2 = 2.941

3-Methylbutyne-1

(large %)

rivative)

2,4-Dimethylpentadiene-1,3

(70%)

(30%)

Table 11. Isomerization

Reactants

Contact Time | Temp. (°C)

Dimethylpentadiene

min. (27.0%)

per (%)

Dimethylpentadiene

min. (6.7%)

2,4-Dimethylpentadiene

3-Ethylpentadiene-1,2

3-Ethylpentadiene-1,2

ALKADIENES

Alkadienes—Continued

Products

% by weight on original

Other Products

2,4-Dimethylpentadiene (71.2%)

Polymers

(67%)

Polymers

3-Ethylpentadiene

3-Ethylpentyne-1 (No details)

Table 12. Isomerization of

Reactants: Non-Allenic Alkadiene	Reactants: Catalyst (Per cent by weight on alkadiene+catalyst)	Contact Time (hours)	Temp. (°C.)
Hexadiene-1,4	Concentrated alcoholic potash (Used 4 to 5 volumes of this reagent per 1 volume of hexadiene-1,4)	6	100
Hexadiene-1,5		10 days	250
Hexadiene-1,5	Pyrex-glass tube	13 sec.	500
Hexadiene-1,5	30% Pd+70% asbestos 30% Pd+70% C	(1 pass) (2 passes)	200 200, 300
Hexadiene-1,5	Al_2O_3		300
Hexadiene-1,5	Al_2O_3		360
Hexadiene-1,5	Al_2O_3	15 drops feed per 92.4 cc. catalyst per min.	365
Hexadiene-1,5	Cr_2O_3	0.02 g. liquid feed per "A" 12 cc. catalyst "B" 24 cc. catalyst "C" 35 cc. catalyst "D" 47 cc. catalyst per minute (catalyst column length study, using "A" 15 cm. catalyst "B" 30 cm. catalyst "C" 45 cm. catalyst "D" 60 cm. catalyst)	225 (all cases)
Hexadiene-1,5	Cr_2O_3	"A" 0.02 g. liquid feed "B" 0.05 g. liquid feed "C" 0.10 g. liquid feed "D" 0.20 g. liquid feed "E" 0.40 g. liquid feed per 35 cc. catalyst per minute (feed velocity study)	225 (all cases)

Non-Allenic Alkadienes

Products (% by weight on original alkadiene)

Pressure (atm.)

Other Products

Hexadiene-2,4 sealed tube (231)

Isomer (10%) Hexadiene-1,5 (67%) (334)

Polymers

(261) (262)

Hexadiene

(CO₂)

Propene

Gaseous alkanes (mostly ethane) (3.55%)

Hexadiene-1,5 (94%)

Hexadiene-2,4 (73.4%) (337)

Hexadiene-2,4 (69%) (338)

Hexadiene-2,4 (82%) (338)

Low-boiling hydrocarbons (50%)

Hexadiene

Small %

Hexadiene-1,5 (11%)

(343) "A" (30.8%) "B" (43.2%) "C" (43.9%) "D" (58.1%)

(CO₂)

"A" (10%) "B" (28%) "C" (28%) "D" (30%)

Hexadiene-1,5 "A" (50.8%) "B" (28.8%) "C" (28.1%) "D" (11.9%)

(343) "A" (43.1%)

Table 12. Isomerization of

Reactants: Non-Allenic Alkadiene	Reactants: Catalyst (Per cent by weight on alkadiene+catalyst)	Contact Time (hours)	Temp. (°C.)
Hexadiene-1,5	Cr_2O_3	0.10 g. liquid feed per 35 cc. catalyst per minute	"A" 225 "B" 250 "C" 275 "D" 300 (temperature effect study)
Hexadiene-1,5	"Floridin"	(6 passes)	225
Hexadiene-1,5	Alcoholic potash	6	170
Hexadiene-2,4	Al_2O_3		360
Hexadiene-2,4	Al_2O_3		450–480
Heptadiene-1,5	Al_2O_3	15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365
2-Methylhexadiene-1,5	Al_2O_3	15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365
3-Methylhexadiene-1,5	Al_2O_3	15 drops feed per 92.4 cc. catalyst per min.	365
2,4-Dimethylpentadiene-1,3 (5.1%) 2,4-Dimethylpentadiene-2,3 (94.9%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	170
2,4-Dimethylpentadiene-1,3 (6.7%) 2,4-Dimethylpentadiene-2,3 (93.3%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	202
2,4-Dimethylpentadiene-1,3	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	204
2,4-Dimethylpentadiene-1,3 (27.0%) 2,4-Dimethylpentadiene-2,3 (73.0%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	205
2,4-Dimethylpentadiene-1,3 (6.7%) 2,4-Dimethylpentadiene-2,3 (93.3%)	"Floridin"	0.1–0.15 g. feed per 7.54 cc. catalyst per min.	206
2,4-Dimethylpentadiene-1,3	"Floridin"		230–235
Octadiene-2,6	Al_2O_3	15 drops feed per 92.4 cc. catalyst per min.	365
3-Methylheptadiene-1,5	Al_2O_3	15 drops feed per 92.4 cc. catalyst per min. (1 pass)	365

Non-Allenic Alkadienes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkadiene): Isomers	Products (Per cent by weight on original alkadiene): Other Products	References
1 (CO_2)	Hexadiene-2,4 "A" (54.0%) "B" (58.2%) "C" (60.9%) "D" (46.7%)	Gases "A" (27%) Gases "B" (18%) Gases and polymers "C" (30%) Gases and polymers "D" (45%) Hexadiene-1,5 "A" (19.0%) "B" (23.8%) "C" (9.1%) "D" (8.3%)	(343)
	Hexadiene-2,4 (41.5%)		(333)
	Hexadiene-2,4 Hexyne-3 (?)	Hexadiene-1,5	(179)
	Hexadiene-1,3 (15%) Hexadiene-1,4 (2%)	Hexadiene-2,4 (83%)	(445)
	Hexadiene-1,3 (15%) Hexadiene-1,4 (20%)	Pentadiene-1,3 (8%) Hexadiene-2,4 (45%)	(445)
	Heptadiene-2,4 (6%) 3-Methylhexadiene-1,5 (8%)	Low-boiling hydrocarbons (small %) Heptadiene-1,5 (58%)	(593a)
	2-Methylhexadiene-2,4 (58%)	Low-boiling hydrocarbons (small %)	(593a)
	4-Methylhexadiene-1,4 or else 2-Ethylpentadiene-1,4 (18%) 4-Methylhexadiene-1,3 or else 3-Methylhexadiene-2,4 (14%)	Low-boiling hydrocarbons (small %)	(593a)
1		2,4-Dimethylpentadiene-1,3 (1.5%) 2,4-Dimethylpentadiene-2,3 (68.5%) Polymers (30%)	(551)
1		2,4-Dimethylpentadiene-2,3 (80%) Polymers (20%)	(551)
1	2,4-Dimethylpentadiene-2,3 (28.0%)	2,4-Dimethylpentadiene-1,3 (5.0%) Polymers (67%)	(551)
1		2,4-Dimethylpentadiene-1,3 (3.8%) 2,4-Dimethylpentadiene-2,3 (71.2%) Polymers (25%)	(551)
1		2,4-Dimethylpentadiene-2,3 (67%) Polymers (33%)	(551)
	2,4-Dimethylpentadiene-2,3		(553)
	Octadiene-3,5 (?) (small %)	Low-boiling hydrocarbons (small %) Octadiene-2,6 (72%)	(593a)
	3-Methylheptadiene-2,4 or else 5-Methylheptadiene-2,4 (4%)	Low-boiling hydrocarbons (small %) 3-Methylheptadiene-1,5 (70%)	(593a)

Table 12. Isomerization of

Reactants: Non-Allenic Alkadiene	Reactants: Catalyst (Per cent by weight on alkadiene+catalyst		Contact Time (hours)	Temp. (°C.)
2,5-Dimethylhexadiene-1,5			12	260
2,5-Dimethylhexadiene-1,5	Steel equipment was used		time of distillation	b.p.
2,5-Dimethylhexadiene-1,5	Al_2O_3			200–225
2,5-Dimethylhexadiene-1,5	Al_2O_3		15 drops feed per 92.4 cc. catalyst per min.	365
2,5-Dimethylhexadiene-1,5	$FeCl_3$			heated
2,5-Dimethylhexadiene-1,5	$MgCl_2$			heated
2,5-Dimethylhexadiene-1,5	"Floridin"		(1 pass)	205–210
2,5-Dimethylhexadiene-1,5	KOH			heated
2,5-Dimethylhexadiene-1,5	Alcoholic potash		4	180
2,6-Dimethylheptadiene-1,5 (Geraniolene)	H_2SO_4 60% H_2O 40%		4	100
2,6-Dimethylheptadiene-1,5 (Geraniolene)	H_2SO_4 (sp.gr. 1.56)	(91%?)	36	15
2,6-Dimethylheptadiene-1,5 (Geraniolene)	H_2SO_4 65% H_2O 35%		3 days	room
2,6-Dimethyloctadiene-2,6 (Linaloolene)	H_2SO_4		20 min.	100
2,6-Dimethyloctadiene-2,6 (Dihydromyrcene)	$H_2SO_4+CH_3CO_2H$			room
2,6-Dimethyloctadiene-2,6 (Dihydromyrcene)	$H_2SO_4+CH_3CO_2H$			"low"
2,6-Dimethyloctadiene-2,6 (Dihydromyrcene)	"50% H_2SO_4" CH_3CO_2H	(5.5%) (63%)	2	40

Non-Allenic Alkadienes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkadiene) Isomers	Other Products	References
	2,5-Dimethylhexadiene-2,4 (41%)		(593a)
1	2,5-Dimethylhexadiene-2,4 (small %)	2,5-Dimethylhexadiene-1,5	(593a)
	2,5-Dimethylhexadiene-2,4		(338)
	2,5-Dimethylhexadiene-1,4 (?) (small %)	Low-boiling hydrocarbons (small %)	(593a)
	2,5-Dimethylhexadiene-2,4(81%)		
	2,5-Dimethylhexadiene-2,4(28%)		(593a)
	2,5-Dimethylhexadiene-2,4(39%)		(593a)
	2,5-Dimethylhexadiene-2,4(70%)		(333)
	2,5-Dimethylhexadiene-2,4 (small %)		(593a)
	2,5-Dimethylhexadiene-2,4	2,5-Dimethylhexadiene-1,5	(179)
	α-Cyclogeraniolene β-Cyclogeraniolene		(583)
1	α-Cyclogeraniolene (large %) β-Cyclogeraniolene (small %)		(632)
1	α-Cyclogeraniolene β-Cyclogeraniolene		(582)
1	1,5,5,6-Tetramethylcyclohexene-1 (Cyclolinaloolene)		(531)
1	1,5,5,6-Tetramethylcyclohexene-1 (Cyclodihydromyrcene)		(532)
1	1,5,5,6-Tetramethylcyclohexene-1 (Cyclodihydromyrcene) (60–65%)	Dihydrolinalyl acetate (32–33.5%)	(515)
1	1,5,5,6-Tetramethylcyclohexene-1 ("α-Cyclomethylgeraniolene")		(147)

Table 13. Isomeriza

Reactants			
Alkapolyene	Catalyst (Per cent by weight on alkapolyene+catalyst)	Contact Time (hours)	Temp. (°C.)
6-Methylheptatriene-1,2,3	K	6	110–120
2,6-Dimethyloctatriene-1,5,7 (Ocimene)		4	b.p.
2,6-Dimethyloctatriene-2,4,6 (Allo-ocimene)	$H_2SO_4+CH_3 . CO_2H$		
2,6-Dimethyloctatriene-2,4,6 (Allo-ocimene)		1 0.5	250–300 320
3-Methylene-7-methyloctadiene-1,6 (Myrcene)		4	300
4,8-Dimethylnonatriene-1,3,7	H_2SO_4 80% H_2O 20% (83.3%)		
2,6-Dimethylundecatriene-2,5,8 (Pseudoionane)	H_2SO_4 2.5% $CH_3 . CO_2H$ 97.5%		b.p.
3,7,11-Trimethyldodecatetraene-1,3,6,10 (?) (α-Farnesene)	$H . CO_2H$		room (?)
3-Methylene-7,11-dimethyldodecatriene-1,6,10 (β-Farnesene)+ 3,7,11-Trimethyldodecatetraene-1,3,6,10 (α-Farnesene)	$H . CO_2H$ 90% H_2O 10% (74.3%)	10 min.	120
3-Methylene-7,11-dimethyldodecatriene-1,6,10 (β-Farnesene)+ 3,7,11–Trimethyldodecatetraene-1,3,6,10 (α-Farnesene)	H_2SO_4 0.5– 1.2% $CH_3 . CO_2H$ 98.8–99.5% (78.4–79.4%)	87	room
2,6,10,15,19,23-Hexamethyltetracosahexaene-2,6,10,14,18,22 (Squalene)	$H . CO_2H$ 98% H_2O 2%	0.5 3 3 days	b.p. b.p. b.p.
2,6,10,15,19,23-Hexamethyltetracosahexaene-2,6,10,14,18,22 (Squalene)	H_2SO_4+acetic anhydride	2.5	b.p.
2,6,10,15,19,23-Hexamethyltetracosahexaene-2,6,10,14,18,22 (Squalene)	$H_2SO_4+C_2H_5OH$	18	b.p.
2,6,10,14,19,23,27,31-Octamethyldotriacontatridecaene-2,6,8,10,12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene solution, or Petroleum ether solution	few days (or sooner if heated)	room (or heated)
2,6,10,14,19,23,27,31-Octamethyldotriacontatridecaene-2,6,8,10,12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene (solvent)	1-2 days	20
2,6,10,14,19,23,27,31-Octamethyldotriacontatridecaene-2,6,8,10,12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene (solvent) (almost 100%)	20 min.	b.p.
2,6,10,14,19,23,27,31-Octamethyldotriacontatridecaene-2,6,8,10,12,14,16,18,20,22,24,26,30 (Lycopene)	Benzene (solvent) (almost 100%)	0.5	b.p.

tion of Alkapolyenes

Pressure (atms.)	Products (Per cent by weight on original alkapolyene) Isomers		Other Products		References
bomb tube	6-Methylhepten-3-yne-1 (K derivative)		H_2		(227)
1 (CO_2)	2,6-Dimethyloctatriene-2,4,6 (Allo-ocimene)	(82%)			(167)
1	2,6-Dimethyloctatriene-1,5,7 (Ocimene)	(10%)	Polymers		(167) (169)
1	Isomeric terpene		Polymers	(38%)	(8)
1	Cyclomyrcene (?)		Polymyrcenes		(243)
1	1,5-Dimethyl-5-allylcyclohexene-1				(226)
1	1,5,5-Trimethyl-6-(1-butenyl)-cyclohexene-1 (α-Ionane)				(304)
1 (?)	d-α-Bisabolene (?) d-β-Bisabolene (?)				(539)
1	α-Bisabolene (?) β-Bisabolene (?)	(54.5%)			(482)
1	Hexahydrocadalene		α-Bisabolyl acetate		(486)
1 1 1	"Dicyclosqualene" "Tricyclosqualene" "Tetracyclosqualene" (respectively)				(244)
1	"Dicyclosqualene" (?)				(244)
1	"Tricyclosqualene" (?)				(244)
1	Neolycopene		Lycopene		(660)
1	Neolycopene	(3%)	Lycopene	(97%)	(660)
1	Neolycopene		Lycopene		(660)
1	Neolycopene		Lycopene		(661)

Table 13. Isomerization

Reactants

Conc. Cat./Time Temp. (°C)

12,14,16,18,20,22,24,26,30 (Lycopene)

3,7,11,15,19,23,27,31-Octamethyl-2,6,8,10,12,14,16,18,20,22,24,26,30-dotriacontatridecaene (Lycopene)

5 min 20

2.0

(velocity study)

12,14,16,18,20,22,24,26,30 (Lycopene)

(solvent) Neolycopene Benzene

(solvent) Neolycopene Benzene

(solvent) 0.25 Neolycopene Benzene

5 min Neolycopene 20

(solvent) 0.5 Benzene

1.5 20

(velocity study)

of Alkapolyenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkapolyene) Isomers		Other Products		References
1	Neolycopene		Lycopene		(661)
1	Neolycopene	(18%)	Lycopene	(82%)	(661)
1	Neolycopene	(29%)	Lycopene	(71%)	
1	Neolycopene	(43%)	Lycopene	(57%)	
1	Neolycopene	(47%)	Lycopene	(53%)	
1	Neolycopene		Lycopene		(661)
1	Lycopene		Neolycopene		(660)
1	Lycopene		Neolycopene		(660)
1	Lycopene	(6%)	Neolycopene	(94%)	(661)
1	Lycopene	(13%)	Neolycopene	(87%)	(661)
1	Lycopene	(19%)	Neolycopene	(81%)	
1	Lycopene	(30%)	Neolycopene	(70%)	

Table 16. Isomerization of

Reactants: Alkyne		Reactants: Catalyst (Per cent by weight on alkyne+catalyst)		Contact Time (hours)	Temp. (°C.)
Propyne Nitrogen Oxygen	(95.7%) (3.4%) (0.6%)	"Pyrex" glass tube used		74.5 sec.	555
Propyne		"Floridin"		7.0 cc. feed per 26.5 cc. catalyst per min.	180
Propyne		"Floridin"		10.4 cc. feed per 26.5 cc. catalyst per min.	231
Propyne		"Floridin"		20.0 cc. feed per 26.5 cc. catalyst per min.	264
Propyne		"Floridin"		10.4 cc. feed per 26.5 cc. catalyst per min.	318
Propyne		"Floridin"		8.0 cc. feed per 26.5 cc. catalyst per min.	326
Propyne		"Floridin"		10.0 cc. feed per 26.5 cc. catalyst per min.	348
Propyne		"Floridin"		10.0 cc. feed per 26.5 cc. catalyst per min.	363
Propyne		Alcoholic potash		12	170–180
Butyne-1		"Floridin"			275
Butyne-1		Pumice			300
Butyne-1		Alcoholic potash		16	170
Butyne-1		Alcoholic potash		"few hours"	170–180
Butyne-2		"Floridin"			278
Butyne-2		"Floridin"			280
Butyne-2		"Floridin"			285
Pentyne-1		Alcoholic potash		24	170
Pentyne-1		Alcoholic potash			30 or 40
Pentyne-2		Na	(40 mole-per cent)	4–5	100

Alkynes, Alkadiynes, and Alkapolyynes

Pressure (atms.)	Products (Per cent by weight on original alkyne) Isomers		Other Products		References
740 mm. Hg	Propadiene	(below 13.6%)	CO_2 CO O_2 N_2 H_2 Alkanes (CH_4, etc.; $n=1.67$ in C_nH_{2n+2}) Ethylene Propene Propyne Liquids (probably propadiene polymers)	(0.37%) (0.39%) (0.67%) (4.27%) (0.062%) (3.5%) (0.87%) (?%) (25.8%) (28%)	(370a)
1	$\frac{\text{Propyne}}{\text{Propadiene}}=4.348$		Polymers	(28%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}}=3.000$		Polymers	(30%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}}=2.484$		Polymers	(30%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}}=1.857$		Polymers	(40%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}}=1.618$		Polymers	(43%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}}=2.030$		Polymers	(50%)	(552)
1	$\frac{\text{Propyne}}{\text{Propadiene}}=1.632$		Polymers	(75%)	(552)
	No isomers		Ethyl isopropenyl ether Propyne		(178)
	Butadiene-1,2				(554)
	Butadiene-1,3				(141a)
	Butyne-2		Butyne-1		(176) (180)
	Butyne-2		Butyne-1		(653)
	Butadiene-1,2 Butyne-1	(10.8%) (13.5%)			(554)
	Butadiene-1,2 Butyne-1	(36.7%) (5.1%)			(554)
	Butadiene-1,2 Butyne-1	(19.3%) (14.1%)			(554)
	Pentyne-2				(176) (180)
	Pentyne-2				(180)
	Pentyne-1 (Na derivative)		Pentene-2 (?)		(177)

Table 16. Isomerization of Alkynes,

Reactants: Alkyne		Reactants: Catalyst (Per cent by weight on alkyne+catalyst)		Contact Time (hours)	Temp. (°C.)
3-Methylbutyne-1		Alcoholic potash		6	150
3-Methylbutyne-1		Activated "Floridin"		0.4 g. feed per min.	270
3-Methylbutyne-1		Al_2O_3			400
3-Methylbutyne-1		Al_2O_3			heated
3-Methylbutyne-1		Al_2O_3			400
Hexyne-1					500
					550
Hexyne-1					600
Hexyne-2		Na			150–160
3,3-Dimethylbutyne-1		Alcoholic potash		16	200
Heptyne-1					600
Heptyne-1	(90.0%)	Pumice			350
Heptyne-2	(10.0%)				
Heptyne-1		Alcoholic potash		24	140–150
Heptyne-1		Alcoholic potash		36	140–150
Heptyne-1 (63% pure)		KOH	(13.5%)	5	200
		C_2H_5OH	(43.2%)		
Heptyne-1 (76% pure)		Soda-lime		5	275
Heptyne-1	(90.0%)	Soda-lime			380
Heptyne-2	(10.0%)				
Heptyne-1	(20.0%)	$NaNH_2$		12	160
Heptyne-2	(80.0%)	Mineral oil (diluent)			
Heptyne-3		$NaNH_2$		4	170
		Pseudocumene (diluent)			
Octyne-1		Alcoholic potash		36	140–150
Octyne-2		Na	(3.84%)	8	"sand bath"
Octyne-2		Na	(16.1%)	(?)	at 100
				and	
				36	at "salt bath"
Octyne-2		$NaNH_2$		1	150
		Pseudocumene (diluent)			
Octyne-3		$NaNH_2$		9	170
		Petroleum (diluent)			
Nonyne-2		$NaNH_2$		2	160
		Petroleum (diluent)			
Dodecyne-1		Alcoholic potash			
Dodecyne-2		Na			
Hexadecyne-1		Alcoholic potash			
Hexadecyne-2		Na			
Hexadiyne-1,4		Alcoholic potash		(?)	(?)
Hexadiyne-1,4		Alcoholic potash		1	100
2,2,9,9-Tetramethyl-5,5,6,6-tetra-*tert*-butylethynyldecadiyne-3,7		Alcohol (solvent)	(96–98%)	1	100

Alkadiynes, and Alkapolyynes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkyne) Isomers		Other Products		References
	3-Methylbutadiene-1,2				(176) (180)
	$\frac{\text{3-Methylbutadiene-1,2}}{\text{3-Methylbutyne-1}}=0.08000$		Polymer	(5%)	(548)
	$\frac{\text{2-Methylbutadiene-1,3}}{\text{3-Methylbutyne-1}}=0.001081$				
40–50 mm. Hg	2-Methylbutadiene-1,3				(639)
reduced	2-Methylbutadiene-1,3				(29)
40–50 mm. Hg	2-Methylbutadiene-1,3	(50%)	3-Methylbutyne-1		(32)
	Hexadiene-1,2		Scission products		(263)
	Hexadiene-1,2 Hexyne-2	 (trace)	Scission products		(263)
	Hexyne-1 (Na derivative)		C_6H_{12}		(177)
No isomers					(176)
	Heptadiene-1,2 Heptyne-2	 (trace)	Scission products		(263)
1	$\frac{\text{Heptyne-1}}{\text{Heptyne-2}}=2.125$				(234)
	Heptyne-2	(100%)			(42)
	Heptyne-2	(100%)			(41)
	Heptyne-2				(24)
	No isomers				(24)
1	Heptyne-1 Heptyne-2	(13.0%) (65.6%)			(234)
	$\frac{\text{Heptyne-1}}{\text{Heptyne-2}}=\frac{64}{36}$				(234)
	Heptyne-1	(70–80%)			(81)
	Octyne-2	(100%)			(41) (42)
	Octyne-1	(9%)	Octyne-2	(large %)	(135)
sealed tube	Octyne-1	(crude, 75%)	Na C_8H_{16}		(43)
	Octyne-1	(80%)			(81)
	Octyne-1	(55%)			(81)
	Nonyne-1	(83%)			(81)
	Dodecyne-2				(323)
	Dodecyne-1				(323)
	Hexadecyne-2				(323)
	Hexadecyne-1				(323)
(?)	Hexadiyne-2,4				(336)
	Hexadiyne-2,4		Hexadiyne-1,5 $C_8H_{12}O$ Resin	 (large %)	(179)
sealed tube	2,2,13,13-Tetramethyl-5,10-di-*tert*-butylethynyl-7,8,-di-*tert*-butyltetradecatetraene-5,6,8,9-diyne-3,11	(40–60%)			(499)

Isomerization of Alkynes

Reactants

Catalyst | Temp.

alkyne

butylethynyldecadiyne-6,7

(solvent)

tetra-(3-methyl-3-ethyl-pent-1-yn-1-yl)-dodecadiyne-4,8

Alkapolyynes—*continued*

Products — per cent by weight on original			
Polymer	Dimer	Isomer	Other Products
[illegible]			2,2,13,13-Tetramethyl-5,10-di-*tert*-butyltetradecatetraene-5,6,8,9-diyne-3,11 (100)
[illegible]			2,2,13,13-Tetramethyl-5,10-di-*tert*-butyltetradecatetraene-5,6,8,9-diyne-3,11 [illegible]
	Dimer, probably 3,14-diethyl-5,12-di-(3-methyl-pent-1-yn-1-yl)-8,9-di-(3-methylpent-3-yl)-hexadecatetraene-6,7,9,10-diyne-4,12 (50%)		

Table 17. Isomerization of Cyclanes and

Reactants: Cyclane	Reactants: Catalyst (Per cent by weight on cyclane+catalyst)	Contact Time (hours)	Temp. (°C.)
Cyclopropane			100
Cyclopropane	Glass tube	4000 cc. feed per 1.75 hour	"glowing red"
Cyclopropane		700 cc. feed per 3.25 hours	360–370
Cyclopropane	"Pyrex" reaction-vessel	8 min.	499.5
Cyclopropane	"Pyrex" reaction-vessel	0.50	499.5
Cyclopropane		20 min.	550
Cyclopropane	Unglazed porcelain tube	27 min.	600
Cyclopropane	Unglazed porcelain tube	51 min.	600
Cyclopropane	Unglazed porcelain tube	54.5 min.	600
Cyclopropane	Unglazed porcelain tube	73 min.	600
Cyclopropane	Glazed porcelain tube, small diameter	31 min.	600
Cyclopropane	Glazed porcelain tube, medium diameter	31 min.	600
Cyclopropane	Glazed porcelain tube, large diameter	31 min.	600
Cyclopropane	Quartz tube	28 min.	600
Cyclopropane	Quartz tube	29 min.	600
Cyclopropane	Quartz tube	43.5 min.	600
Cyclopropane	Al_2O_3		350–360
Cyclopropane	Al_2O_3	600 cc. feed per 1.75 hour	370–385
Cyclopropane	Pt black Air, moisture	5 months	room
Cyclopropane	Pt black Air, moisture	120	100
Cyclopropane	Pt black (Levy's)	700 cc. feed per 1.50 hour	200
Cyclopropane	Pt black (Levy's)	500 cc. feed per 1.75 hour	315
Cyclopropane	Pt asbestos		400
Cyclopropane	Fe filings		600
Cyclopropane	I_2	18	279.2
Cyclopropane	$ZnCl_2$ (anhydrous)	0.5	below b.p. of catalyst

Cyclanes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original cyclane) Isomers		Other Products		References
	Propene	(15–18%)			(577)
	Propene	(large %)			(576)
1	Propene	(1–2%)			(279)
37.91 cm. Hg	Propene	(25%)			(104)
37.22 cm. Hg	Propene	(65%)			(104)
1	Propene	(75%)	H_2+alkane gas C_2H_4 Cyclopropane	(14% by vol.) (7% by vol.) (4%)	(62)
1	Propene	(1.5%)	Cyclopropane (?) Polymer (?)		(590)
1	Propene	(61.5%)	Cyclopropane (?) Polymer (?)		(590)
1	Propene	(70.0%)	Cyclopropane (?) Polymer (?)		(590)
1	Propene	(86.2%)	H_2 CH_4 Hexene-2 (?)	(1.2% by vol.) (1.2% by vol.)	(590)
1	Propene	(7.9%)	Cyclopropane (?) Polymer (?)		(590)
1	Propene	(16.0%)	Cyclopropane (?) Polymer (?)		(590)
1	Propene	(50.2%)	H_2 CH_4 Cyclopropane (?) Polymer (?)	(0.7%? by vol.) (1.4% by vol.)	(590)
1	Propene	(76.0%)			(590)
1	Propene	(92.8%)			(590)
1	Propene	(96.5%)			(590)
1	Propene	(15%)			(279)
1	Propene	(20%)			(279)
	Propene	(19–30%)			(577)
	Propene	(45%)			(577)
1	Propene	(4–5%)			(279)
1	Propene	(29%)			(279)
	Propene	(70%)			(472)
	Propene	(50–70%)	Cyclopropane		(270) (273)
Initially: 93.2 mm. Hg (cyclopropane) + 86.6 mm. Hg (iodine vapor) In 3 hours: 144.4 mm. Hg In 18 hours: 177.5 mm. Hg	Propene	(small %)	$CH_2I . CH_2 . CH_2I$		(426)
1	Propene	(40%)	Cyclopropane	(60%)	(62)

Table 17. Isomerization of Cyclanes and

Reactants: Cyclane		Reactants: Catalyst (Per cent by weight on cyclane+catalyst)		Contact Time (hours)	Temp. (°C.)
Methylcyclopropane		Al_2O_3		2000 cc. feed per 1.33 hour or 2500 cc. feed per 3 hours or 2450 cc. feed per 3.33 hours or 2240 cc. feed per 3.33 hours	340–356 340–355 350–358 350–360
1,1-Dimethylcyclopropane		Al_2O_3		8 g. feed per 71 min.	340–345
Ethylcyclopropane		Al_2O_3-asbestos		5 g. feed per 2 hours	300–310
Methylcyclobutane		Al_2O_3		7 g. feed per 2 hours	400
Cyclopentane		$AlCl_3$	(23%)	8	b.p.
Methylcyclopentane		Sulfur compounds of Co and of Mo	(15.8%)	1	500
Methylcyclopentane Cyclohexane (various mixtures)		$AlBr_3+HBr$ (gas), or $AlCl_3$ (partially hydrated)			25.1
Methylcyclopentane Cyclohexane (various mixtures)		$AlBr_3+HBr$ (gas), or $AlCl_3$ (partially hydrated)		24–48	61.0
Methylcyclopentane Cyclohexane (various mixtures)		$AlBr_3+HBr$ (gas), or $AlCl_3$ (partially hydrated)			99.5
Methylcyclopentane Cyclohexane	(30%) (70%)	$AlBr_3$ HBr (gas)	(23.9%) (1.4%)	24	61
Methylcyclopentane		$AlCl_3$ HCl (gas)		10	20
Methylcyclopentane		$AlCl_3$ (partially hydrated)	(14.0%)	21.5	61
Methylcyclopentane Cyclohexane	(15%) (85%)	$AlCl_3$ (partially hydrated)	(19.3%)	51	61
Methylcyclopentane		$AlCl_3$ H_2O	(20.9%) (0.7%)	3	b.p.
Methylcyclopentane		$AlCl_3$ HCl (gas)		10	80
Methylcyclopentane		$AlCl_3$ HCl (gas)		10	80
Methylcyclopentane		$AlCl_3$	(34.6%)	20–22	b.p.
Methylcyclopentane		$AlCl_3$ H_2O	(30.5%) (0.8%)	30	b.p.

Cyclanes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclane) Isomers	Other Products	References
1	Butene-2 (large %) Isobutene (small %)	Dimer of isobutene (10%)	(140)
1			
1			
1			
1	2-Methylbutene-2 (93.75%)		(279)
1	Pentene-2		(479)
1	2-Methylbutene-1 3-Methylbutene-1 Pentene-2		(480)
1	No isomers	Cyclopentane unchanged	(129)
100 (H_2)	Cyclohexane (small %)	Methylcyclopentane (large %)	(452)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=7.333$ at "equilibrium"		(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.651$ at "equilibrium"		(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=1.174$ at "equilibrium"		(441)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.673$		(441)
autoclave	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=8.00$ at "equilibrium" Cyclohexane (88.0%)	Low-boiling hydrocarbons (1.0%) Methylcyclopentane (11.0%)	(529a)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=1.632$		(441)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.651$		(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=2.89$ Cyclohexane (58.6%)	Low-boiling product (1.8% by volume) High-boiling product (9.5% by volume)	(215)
autoclave	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.27$ at "equilibrium" Cyclohexane (76.6%)	Methylcyclopentane (23.4%)	(529a)
autoclave	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.40$ at "equilibrium" Cyclohexane (76.5%)	Low-boiling hydrocarbons (0.6%) Methylcyclopentane (22.5%)	(529a)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=5.25$		(595)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.386$		(399)

Table 17. Isomerization of Cyclanes and

Reactants: Cyclane	Reactants: Catalyst (Per cent by weight on cyclane+catalyst)		Contact Time (hours)	Temp. (°C.)
1,2-Dimethylcyclopentane	$AlCl_3$	(31.2%)		100–104
Ethylcyclopentane	$AlCl_3$ H_2O	(17.3%) (0.5%)	18	50
Ethylcyclopentane	$AlCl_3$	(31.5%)	20	110–115
Propylcyclopentane	$AlCl_3$ H_2O	(16.6%) (0.4%)	18	50
Propylcyclopentane	$AlCl_3$	(28.4%)	20	140–145
Isopropylcyclopentane	$AlCl_3$ H_2O	(15.9%) (0.4%)	18	50
Isopropylcyclopentane	$AlCl_3$	(28.3%)	20 ?	125–130
n-Butylcyclopentane	$AlCl_3$ H_2O	(15.4%) (0.4%)	18	50
n-Butylcyclopentane	$AlCl_3$	(26%)	20–24	160–165
sec-Butylcyclopentane	$AlCl_3$ H_2O	(14.5%) (0.4%)	18	50
tert-Butylcyclopentane	$AlCl_3$ H_2O	(22.6%) (0.6%)	18	50
n-Amylcyclopentane	$AlCl_3$	(24.1%)	20	150–155
Cyclohexane	Al_2O_3	(6.98%)	4	500–510
Cyclohexane	Al_2O_3 in quartz tube		0.06 g. feed per 28.3 cc. catalyst per minute	500
Cyclohexane	$Al_2O_3+ZnCl_2$ in quartz tube		0.06 g. feed per 28.3 cc. catalyst per minute	500
Cyclohexane	$Al_2O_3+H_3PO_4$ in quartz tube		0.06 g. feed per 28.3 cc. catalyst per minute	500
Cyclohexane	BeO			450
Cyclohexane	Quartz tube		0.06–0.1 g. feed (?) per 84.8 cc. reaction-space per minute	550
Cyclohexane	TiO_2			450
Cyclohexane	Copper chromite (Adkins')		0.6 g. feed per 28.3 cc. catalyst per minute	500
Cyclohexane	Copper chromite (Adkins')		0.1 g. feed per 28.3 cc. catalyst per minute	500

Cyclanes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclane): Isomers	Products (Per cent by weight on original cyclane): Other Products	References
1	Methylcyclohexane (96.7%)		(598c)
sealed tube	Methylcyclohexane (90%)		(440)
	Methylcyclohexane (83.4%)	Ethylcyclopentane (2.6%)	(597)
sealed tube	1,3-Dimethylcyclohexane (95.3%)		(440)
1	1,3- and 1,4-Dimethylcyclohexanes (72.2%)	Alkanes (1.4%) Propylcyclopentane	(598)
sealed tube	1,3-Dimethylcyclohexane (96.3%)		(440)
1	1,3- and 1,4-Dimethylcyclohexanes (70.2%)	Alkanes Cyclopentane derivatives } (17%)	(598a)
sealed tube	1,3,5-Trimethylcyclohexane (96.4%)		(440)
1	1,2,4-Trimethylcyclohexane (below 72%)	Alkanes (5.7%) Cyclopentane derivatives (12.3%)	(596)
sealed tube	1,3,5-Trimethylcyclohexane (98%)		(440)
sealed tube	1,3,5-Trimethylcyclohexane (60%)		(440)
1	Tetramethylcyclohexanes (?)	Low-boiling hydrocarbons High-boiling hydrocarbons	(598b)
110–120	Methylcyclopentane (small %)	Hydrogen Methane Other hydrocarbons	(275)
1	Not considered	Gas with 75.04% H_2, 2.2% saturated hydrocarbons, and 4.1% unsaturated hydrocarbons Catalyzate with 4.2% unsaturated hydrocarbons, 66.3% cyclanes, and 29.5% aromatics	(297a)
1	Not considered (The catalyzate had 5.1% of iso-compounds in cyclanes and aromatics.)	Gas with 92.2% H_2, 0.0% saturated hydrocarbons, and 0.8% unsaturated hydrocarbons Catalyzate with 5.3% unsaturated hydrocarbons, 66.2% cyclanes, and 28.5% aromatics	(297a)
1	Not considered (The catalyzate had 5.5% of iso-compounds in alkanes and cyclanes.)	Catalyzate with 3.7% alkanes, 4.3% unsaturated hydrocarbons, 87.7% cyclanes, and 5.3% aromatics	(297a)
1	No isomers	Cyclohexane (100%)	(12a)
1	No isomers	Cyclohexane (100%)	(297a)
1	No isomers	Cyclohexane (large %) Benzene (small %)	(12a)
1	Not considered (The catalyzate had 2.4% of iso-compounds in alkanes and cyclanes.)	Gas with 96.18% H_2 Catalyzate with 1.2% alkanes, 2.7% unsaturated hydrocarbons, 28.8% cyclanes, and 57.3% aromatics	(297a)
1	Not considered (The catalyzate had 2.5% of iso-compounds in alkanes and cyclanes.)	Gas with 95.8% H_2 Catalyzate with 2.07% alkanes, 2.3% unsaturated hydrocarbons, 16.94% cyclanes, and 77.7% aromatics	(297a)

Table 17. Isomerization of Cyclanes and

Reactants: Cyclane	Reactants: Catalyst (Per cent by weight on cyclane+catalyst)	Contact Time (hours)	Temp. (°C.)
Cyclohexane	Sulfur compounds of Co and of Mo (15.8%)	1	450
Cyclohexane	Sulfur compounds of Co and of Mo (15.8%)	1	500
Cyclohexane	MoS_2 (9.0%)	26	400
Cyclohexane	MoS_2		400
Cyclohexane	MoS_2		500
Cyclohexane	Molybdenum sulfide *via* addition of H_2SO_4 to solution of molybdenum oxide in ammonium sulfide. Supported (1 part) on Japanese acid clay (5 parts) that was prior-activated by mineral acids.	145 cc. feed per 717 cc. catalyst per hour	379
Cyclohexane	Molybdenum sulfide *via* addition of H_2SO_4 to solution of molybdenum oxide in ammonium sulfide. Supported (1 part) on Japanese acid clay (5 parts) that was prior-activated by mineral acids.	113 cc. feed per 717 cc. catalyst per hour	411
Cyclohexane	Molybdenum sulfide *via* addition of H_2SO_4 to solution of molybdenum oxide in ammonium sulfide. Supported (1 part) on Japanese acid clay (6 parts) that was prior-activated by mineral acids (24.1%) H_2 (7.1%)	1	430
Cyclohexane	MoO_3 (8.2%) Sulfur (1.4%) H_2 (8.4%)	1	430
Cyclohexane	MoO_3 (8.2%) Sulfur (1.4%) H_2 (8.4%)	1	430
Cyclohexane	MoO_3 (8.1%) Sulfur (1.4%) H_2 (9.4%)	2	439
Cyclohexane	Potash-glass tube	6–8	300
Cyclohexane	Potash-glass tube	8	330
Cyclohexane	Soda-glass tube	8	330
Cyclohexane	Alkali-glass tube	3 days	350
Cyclohexane	Alkali-glass tube	3 days	420
Cyclohexane	$AlBr_3$ (51.4%)	12	180

Cyclanes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclane) Isomers	Other Products	References
100 (H_2)	Methylcyclopentane (small %)	Cyclohexane (large %) C_7H_{14} (small %)	(452)
100 (H_2)	Methylcyclopentane (large %)	Cyclohexane (small %)	(452)
140–350 (H_2)	Methylcyclopentane (62% of *recovered* hydrocarbons)	*n*-Hexane Isohexanes	(454)
300? (H_2)	Methylcyclopentane	*n*-Hexane Isohexanes	(453b)
300? (H_2)	Methylcyclopentane	Gases Isohexanes Unsaturated hydrocarbons Aromatics	(453b)
200 (H_2)	Methylcyclopentane (33.4%)	Cyclohexane (60.9%) Unsaturated hydrocarbons (0.8%) Aromatics (0.1%)	(4) (5b)
200 (H_2)	Methylcyclopentane (67.7%)	Cyclohexane (17.6%) Unsaturated hydrocarbons (0.4%) Aromatics (0.6%)	(4)
242 (H_2)	Methylcyclopentane (17.2%)	H_2 (99.74% was recovered) Low-boiling fractions (0.84%) Unsaturated hydrocarbons in 77–81° b.p. fraction (0.27%) Aromatic hydrocarbons in 77–81° b.p. fraction (0.18%) Cyclohexane (72.9%) High-boiling fraction (0.28%) Distillation residue (1.5%)	(5a)
240 (H_2)	Methylcyclopentane (15.3%)	Cyclohexane (75.8%) Saturated hydrocarbons (2.6%) Unsaturated hydrocarbons (0.2%) Aromatics (0.6%)	(5)
240 (H_2)	Methylcyclopentane (15.3%)	H_2 (99.70% was recovered) CH_4 (0.2%) Low-boiling fraction (0.47%) Unsaturated hydrocarbons in 77–80° b.p. fraction (0.18%) Aromatic hydrocarbons in 77–80° b.p. fraction (0.55%) Cyclohexane (75.8%) High-boiling fraction (0.95%) Distillation residue (1.2%)	(5a)
262–261 (H_2)	Methylcyclopentane (10.9%)	Cyclohexane (80.5%) Saturated hydrocarbons (2.4%) Unsaturated hydrocarbons (0.4%) Aromatics (0.0%)	(5)
sealed tube	Methylcyclopentane (small %)	Cyclohexane (large %)	(16)
sealed tube	Methylcyclopentane (large %)	Cyclohexane (large %)	(16)
sealed tube	No isomers	Cyclohexane (100%)	(16)
sealed tube	No isomers	Cyclohexane (100%)	(547)
sealed tube	Methylcyclopentane (5%)	Cyclohexane (95%)	(547)
	No isomers	"Cyclohexane"	(674)

Table 17. Isomerization of Cyclanes and

Reactants: Cyclane	Reactants: Catalyst (Per cent by weight on cyclane+catalyst)		Contact Time (hours)	Temp. (°C.)
Cyclohexane	$AlBr_3$	(51.4%)	24	100
Cyclohexane	$AlBr_3$ HBr (gas)	(24.1%) (1.3%)	3	61
Cyclohexane	$AlBr_3$ HBr (gas)	(25.1%) (1.5%)	48	61
Cyclohexane	$AlCl_3$	(66.7%)	48	at room (then heated to b.p.)
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ H_2O	(28%) (0.9%)	few minutes at b.p. then 3–4 weeks at 25	
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ (partially hydrated), or $AlBr_3$+HBr (gas)			25.1
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ H_2O	(28%) (0.9%)	few minutes at b.p. then 3–4 weeks at 35	
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ H_2O	(28%) (0.9%)	few minutes at b.p. then 3–4 weeks at 45	
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ H_2O	(28%) (0.9%)	few minutes at b.p. then 3–4 weeks at 55	
Cyclohexane	$AlCl_3$ (partially hydrated)	(13.7%)	23	61
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ (partially hydrated), or $AlBr_3$+HBr (gas)		24–48	61.0
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ H_2O	(28%) (0.9%)	few minutes at b.p. then 3–4 weeks at 65	
Cyclohexane	$AlCl_3$ H_2O	(29.8%) (0.8%)	3	b.p.
Cyclohexane	$AlCl_3$ H_2O	(29.8%) (0.8%)	16	b.p.
Cyclohexane	$AlCl_3$ H_2O	(20.4%) (0.4%)	3	b.p.
Cyclohexane	$AlCl_3$ H_2O	(20.4%?) (0.4%?)	3 (?)	b.p. (?)
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ H_2O	(28%) (0.9%)	2	77.4
Cyclohexane Methylcyclopentane (various mixtures)	$AlCl_3$ (partially hydrated), or $AlBr_3$+HBr (gas)			99.5
Cyclohexane	$AlCl_3$ HCl (gas)		10	110

Cyclanes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclane): Isomers	Products: Other Products	References
1	Methylcyclopentane (?) Dimethylcyclobutane (3.57%)	Alkanes (?) Cyclohexane (?)	(675)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=7.197$		(441)
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.310$		(441)
1	Methylcyclopentane	HCl Cyclohexane Resins (large %)	(16)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=7.00$		(215)
1	average value at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=7.333$ at "equilibrium"		(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=5.90$		(215)
1	average value at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=5.18$		(215)
1	average value at "equilibrium"		
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=4.20$		(215)
1	average value at "equilibrium"		
sealed tube	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=1.462$		(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.651$ at "equilibrium"		(441)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.67$ at "equilibrium"		(215)
1	Methylcyclopentane (below 5%)	Cyclohexane *n*-Hexane (?)	(399)
1	Methylcyclopentane (20.6%)	Cyclohexane	(643a)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=3.95$ (?)	Low-boiling product High-boiling product	(215)
1 (?)	Methylcyclopentane (16.0%)	Isohexanes (0.28%) Cyclohexane Methylcyclohexane (0.13%) 1,3-Dimethylcyclohexane (0.16%) Dimethyldicyclopentyl } (0.23%) Dicyclohexyl }	(215)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=2.91$ average value at "equilibrium"		(215)
1	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=1.174$ at "equilibrium"		(441)
autoclave	$\frac{\text{Cyclohexane}}{\text{Methylcyclopentane}}=1.86$ at "equilibrium" Methylcyclopentane (31.9%)	Low-boiling hydrocarbons (5.6%) Cyclohexane (59.3%) High-boiling hydrocarbons (3.2%)	(529a)

Isomerization of Cyclohexane and Methylcyclohexane

Catalyst	Reactants	Temp. (°C)	Contact (hours)
[illegible]	Cyclohexane, HCl (gas)	[illegible]	g. cyclohexane per 56.5 cc. catalyst per hour
[illegible]	Cyclohexane	[illegible]	10
[illegible]	Cyclohexane, HCl (gas)	[illegible]	10
[illegible]	Cyclohexane, HCl (gas)	[illegible]	10
[illegible]	Cyclohexane	130–160	3
[illegible]	Cyclohexane	[illegible]	24
[illegible]	Methylcyclohexane (unstable form)	[illegible]	7 days
[illegible]	Methylcyclohexane (unstable form via 2-Methylcyclohexanone semicarbazone)	[illegible]	3 days
[illegible]	Methylcyclohexane (unstable form via 4-Methylcyclohexanone semicarbazone)	[illegible]	5 days
[illegible]	Methylcyclohexane (unstable form)	[illegible]	[illegible]
[illegible]	Methylcyclohexane	[illegible]	[illegible]
[illegible]	Methylcyclohexane (5% HCl (gas))	[illegible]	10
[illegible]	Methylcyclohexane	[illegible]	3
[illegible]	Methylcyclohexane	[illegible]	7
[illegible]	Methylcyclohexane	[illegible]	10

Products (% by weight on original)

Principal Products | Other Products

(above fractions were ... the initial product)

Cyclohexane

Methylcyclopentane

High-boiling hydrocarbons

"No isomerization"

Methylcyclopentane

cyclohexane)

Dimethylcyclohexane

Dimethyldicyclopentyl

Dicyclohexyl

Methylcyclohexane

total about 3.5% by volume

(CO₂)

Methylcyclohexane

Isomerization of Cyclanes

Cyclane	Temp. (°C.)	Catalyst (per cent by weight on cyclane + catalyst)	Contact Time
1,2-Dimethylcyclohexane	80	(5%) $AlCl_3$ (15%) HCl (gas)	16
cis-1,2-Dimethylcyclohexane	175	Ni	
1,2-Dimethylcyclohexane	115–120	(3%) $AlCl_3$	7–8 (?)
1,3-Dimethylcyclohexane	115–120	(3%) $AlCl_3$	7–8 (?)
cis-1,4-Dimethylcyclohexane	175	Ni	
1,4-Dimethylcyclohexane	115–120	(3%) $AlCl_3$	7–8 (?)
Ethylcyclohexane	135–140	(10%) $AlCl_3$ (anhydrous)	
Ethylcyclohexane	100	(20%) $AlCl_3$	1
Ethylcyclohexane	100	(20%) $AlCl_3$	2
Ethylcyclohexane	115–120	(3%) $AlCl_3$	8
Ethylcyclohexane	120–130	(20%) $AlCl_3$	1.5
Ethylcyclohexane	115–120	(20%) $AlCl_3$	4
Ethylcyclohexane	115–120	(20%) $AlCl_3$	5
1,3,5-Trimethylcyclohexane	140	(10%) $AlCl_3$	20
Propylcyclohexane	135–145	(3%) $AlCl_3$	7.5
Isopropylcyclohexane	130–145	(3%) $AlCl_3$	7.5
n-Butylcyclohexane	150–160	(3%) $AlCl_3$	8
[illegible]-Butylcyclohexane	140–150	(20%) $AlCl_3$	7
tert-Butylcyclohexane	150–160	(20%) $AlCl_3$	7.5
[illegible]-Butylcyclohexane	130–140	(20%) $AlCl_3$	4
1,3-Diethylcyclohexane	120–130	(20%) $AlCl_3$	4
n-Amylcyclohexane	130–155	(25%) $AlCl_3$	7
Isoamylcyclohexane	130–140	(18.7%) $AlCl_3$	5

Alkyl Chain with Saturated Products

Products by weight on original olefin (Amount) / Other Products

1,2-Dimethylcyclohexane

1,3-Dimethylcyclohexane

No isomers (crude) (?) (571)

1,4-Dimethylcyclohexane

(crude, 88%)

Alkylcyclohexanes

1,3,5-Trimethylcyclohexane

Unsaturated

Tetramethylcyclohexanes (80–85%)

Saturated fraction, b.p. 110–159°

Saturated fraction, b.p. 100 – 110° (probably methylcyclohexane)

Saturated fraction, b.p. 160 – 179° (probably tetramethylcyclohexanes) (25%)

High-boiling residue

Saturated fraction, b.p. 95 – 105° (probably methylcyclohexane) (5%)

Saturated fraction, b.p.

Isomerization of Cyclanes

Cyclane	Reactants	Temp. (°C.)	Contact Time
Methylenecyclopropane		350	
Methylenecyclobutane		300	10.0 g. feed per 30 min.
Methylenecyclobutane		300	
Methylenecyclobutane	300 °C. on asbestos		
Methylenecyclobutane	ZnBr(OH) Dilute alcohol	180–185	
Methylenecyclobutane	Alkylation		
Methylenecyclobutane	H_2SO_4 HBr (trace) (used individually)	at 395–400	7.5 g. feed per 0.75 hour
		or at 400–405	13.5 g. feed per 0.75 hour
		or at 410–430	7.5 g. feed per 0.50 hour
Isopropylidenecyclobutane	1 volume H_2SO_4, 1 volume C_2H_5OH	100	
Methylenecyclohexane			
Methylenecyclohexane			
Methylenecyclohexane			
1,3-Methylenecyclohexane			
Methylenecyclohexane	C_2H_5OH		
Ethylidenecyclohexane	1 volume H_2SO_4, 1 volume C_2H_5OH (66.7% by volume)	100	
Vinylidenecyclohexane		170	
Vinylidenecyclohexane			
Allylcyclohexane	Quartz tube heated	500–650	
Propylidenecyclohexane	H_2SO_4, C_2H_5OH heated		
Isopropylidenecyclohexane	H_2SO_4, C_2H_5OH	100	
Methylisopropylidenecyclohexane	1 volume H_2SO_4, 1 volume C_2H_5OH	100	

WITH UNSATURATED SIDE-CHAIN

With Unsaturated Side-Chain

Products		
Percent by weight on original (?)	Yield of Isomers	Other Products
Butadiene-1,3	(372)	
1-Methylcyclobutene-1	(137)	
1-Methylcyclobutene-1	(239)	
1-Methylcyclobutene-1	(130)	
1-Methylcyclobutene-1	(130)	
1-Methylcyclobutene-1	(642)	Residue
1-Methylcyclobutene-1	(238)	
2-Methylbutadiene-1,3	(140)	p-Cymene Polymers
1		
1		
1-Isopropylcyclopentene-1	(630)	
1-Methylcyclohexene-1 (41.7%)	(181)	
1-Methylcyclohexene-1 (71.1%)	(181)	
1-Methylcyclohexene-1 (75.0%)	(181)	
1-Methylcyclohexene-1	(663)	
1-Methylcyclohexene-1	(628)	
1-Ethylcyclohexene-1	(629)	
1-Vinylcyclohexene	(109)	
Cyclohexylacetylene (?) (tentative)	(109)	
Propylcyclohexane	(202)	Decomposition products
(90%) Propylcyclohexene	(628)	
1-Isopropylcyclohexene-1	(631)	
1-Methyl-3-isopropylcyclohexene-1 (?) (20%)	(627)	
dl-1-Methyl-4-isopropyl-	(624)	

Isomerization of Cycloalkynes

Reactants		Catalyst	Temp. (°C)	Cont. time
5-Cyclohexylpentyne-2.5	Petroleum (diluent)		(61%)	
6-Cyclohexylhexyne-2	Petroleum (diluent)			
6-Cyclohexylhexyne-22	Petroleum (diluent)			

Table 19. Isomeriza

Reactants	Catalyst	Temp.	Cont. time
Spiro[4.5]decane		120	per min.
Spiro[4.5]decane	drops		per min.
Spiro[4.5]decane	Isomer		without the isomerization (CO_2 atmosphere)

... Side Chain (Continued)

Products (% by weight on original cycloalkane)	Pressure	Isomer	Other Products	Reference
Cyclohexylpentyne-1 (70%)				(81)
Cyclohexylpentyne-2 (95%)				
Cyclohexylhexyne-1 (80%)				(83)
Cyclohexylhexyne-2 (10%)				(81)

... tion of Spiranes

Products (% by weight on original cycloalkane)	Pressure	Isomer	Other Products	Reference
Isomer, b.p. 185.5–186° at 750 mm. Hg, d_4^{20} = 0.8730, n_D^{20} = 1.4683				(671e)
Isomer			Spiro[4.5]decane (CO_2)	(671e)
Isomer, b.p. 185–186° at 748 mm. Hg, d_4^{20} = 0.8725, n_D^{20} = 1.4691				(671e)

Table 20. Isomerization of Bicyclanes and

Reactants: Bicyclane	Reactants: Catalyst (Per cent by weight on bicyclane+catalyst)		Contact Time (hours)	Temp. (°C.)
cis-Bicyclo[3.3.0]octane	$AlCl_3$ (sublimed)	(28.6%)	2–48	room
cis-Bicyclo[4.3.0]nonane (*cis*-Hydrindane)	$AlBr_3$ (anhydrous)	(43%)	12	100
Methylhydrindane	MoS_3			high
cis-Bicyclo[4.4.0]decane (*cis*-Decalin)	Steel autoclave used		2	360–370
cis-Bicyclo[4.4.0]decane with some *trans*-Bicyclo[4.4.0]decane	Ni-Co-Al alloy		1	300
cis-Bicyclo[4.4.0]decane	Ni-Co-Al alloy		1.5	300
cis-Bicyclo[4.4.0]decane	MoS_3 Steel autoclave used	(9.09%)	1.5	320–325
cis-Bicyclo[4.4.0]decane	MoS_3 Steel autoclave used	(9.09%)	2	360–370
cis-Bicyclo[4.4.0]decane	MoS_3 Steel autoclave used	(9.09%)	1	425–430
cis-Bicyclo[4.4.0]decane	$AlBr_3$	(39.3%)	12	100
cis-Bicyclo[4.4.0]decane	$AlBr_3$ HBr	(31.25%)		room
cis-Bicyclo[4.4.0]decane	$AlCl_3$ (technical)	(28.6%)	22	room
cis-Bicyclo[4.4.0]decane	$AlCl_3$	(24.3%)	12	100
cis-Bicyclo[4.4.0]decane	$AlCl_3$ (technical)	(50%)	14	100
cis-Bicyclo[4.4.0]decane	$AlCl_3$	(10%)	time of distillation	175–210
cis-Bicyclo[4.4.0]decane (25.0%) *trans*-Bicyclo[4.4.0]decane (75.0%) ("Decalin")	$AlCl_3$	(24.2%)	24	130
trans-Bicyclo[4.4.0]decane	MoS_3			high
cis-9-Methyldecalin	$AlCl_3$			20
1,10-Dimethyldecalin (mainly *cis*)	$AlCl_3$	(50%)	2 days	room
3,6-Dimethyl-9-isopropylbicyclo-[5.3.0]decane (β-Vetivane)	$AlCl_3$	(44.4%)	72	room

Bicyclanes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original bicyclane): Isomers	Other Products	References
1	Bicyclo[3.2.1]octane		(37)
1	*trans*-Bicyclo[4.3.0]nonane Unidentified isomer	$AlBr_3$+hydrocarbon complex $C_{27}H_{24}$ (m.p. 192–193°)	(674)
	Dimethylbicyclooctane		(293)
100–230 (H_2)	No isomers	*cis*-Bicyclo[4.4.0] decane	(449)
50 (H_2)	*trans*-Bicyclo[4.4.0]decane		(545a)
50 (H_2)	*trans*-Bicyclo[4.4.0] decane	H_2 CH_4	(545a)
95–193 (H_2)	No isomers	*cis*-Bicyclo[4.4.0]decane	(449)
100–230 (H_2)	*trans*-Bicyclo[4.4.0]decane (52%)		(449)
100–245 (H_2)	*trans*-Bicyclo[4.4.0]decane (40%) Dimethylbicyclo[3.3.0]octane (8%)	Decomposition products	(449)
1	*trans*-Bicyclo[4.4.0]decane (6%) Isomer (b.p. 170–175°) (4%)		(673)
1	*trans*-Bicyclo[4.4.0]decane	$C_{10}H_{18}(AlBr_3)_2$	(674)
1	*trans*-Bicyclo[4.4.0]decane (85%)		(676)
1	*trans*-Bicyclo[4.4.0]decane	Lower-boiling products	(676)
1	*trans*-Bicyclo[4.4.0]decane (42.2%)	Lower-boiling products (50%)	(676)
1	*trans*-Bicyclo[4.4.0]decane Dimethylbicyclo[3.3.0]octane	Alkanes Cyclopentanes Cyclohexanes	(677)
1	*trans*-2,6-Dimethylbicyclo[3.3.0]-octane	Cyclohexane Methylcyclohexane 1,3,5-Trimethylcyclohexane Decalins, mainly *trans* (50–70%)	(291)
	Dimethylbicyclooctane		(293)
1	*trans*-9-Methyldecalin		(252)
1	*trans*-1,10-Dimethyldecalin		(351)
1	More-stable isomer (82.7%)		(395b)

Table 21. Isomerization of Bicy

Reactants: Bicyclane	Catalyst (Per cent by weight on bicyclane+catalyst)		Contact Time (hours)	Temp. (°C.)
d-Sabinene	Dilute (1 : 7) H_2SO_4		4	b.p.
d-Sabinene	"Dilute H_2SO_4"			heated
d-Sabinene	H_2SO_4 C_2H_5OH			heated
d-Sabinene	"50% H_2SO_4" $CH_3 . CO_2H$	(6.5%) (46.7%)	0.25	room to 50
d-Sabinene	$H . CO_2H$	(50%)	0.25	−20
Camphene	"Suprax" glass			360–370
Camphene	"89% H_3PO_4"	(33.3%)	10	200
dl-α-Fenchene	H_2SO_4 $KHSO_4$	(trace) (36.3%)	7 min.	b.p.
dl-α-Fenchene	$KHSO_4$ H_2SO_4 (?)	(36.3%?)	15 min.	b.p.
d-β-Fenchene (Dd-Fenchene, probably with some γ-fenchene)	H_2SO_4 C_2H_5OH (solvent)	(small %)	several	heated
d-β-Fenchene (probably with some γ-fenchene)	2-Normal H_2SO_4 C_2H_5OH (solvent)	(10.7%) (53.1%)	1.5	b.p.
d-β-Fenchene (probably with some γ-fenchene)	H_2SO_4 $KHSO_4$ C_2H_5OH (solvent)	(trace) (5.4%) (56.3%)	2	b.p.
β-Pinene	"Suprax" glass			345–350
d-β-Pinene			175 g. β-pinene feed per hour	400–405
l-β-Pinene	$Pd+H_2$		1	room
l-β-Pinene	$Pd+H_2$		7	room
β-Pinene	Fuller's earth	(28.6%)	1.5	b.p.
β-Pinene	$NiSO_4 . H_2O$	(2.44–2.91%)		140
β-Pinene	$NiSO_4 . H_2O$	(1.96–2.91%)		140
β-Pinene	$NiSO_4 . H_2O$			heated
β-Pinene β-Pinene	Acid-treated porcelain Acid-treated broken clay ware Acid-treated permutite Acid-treated bleaching earth Acid-treated fuller's earth (used individually)			150 heated
β-Pinene	Acid-treated permutite Acid-treated silica gel (used individually)			90
β-Pinene	HCl-treated ammonium tungstate Steam-treated ammonium tungstate HNO_3-treated ammonium tungstate HCl-treated sodium tungstate Steam-treated ammonium vanadate (used individually)			heated

clanes with Unsaturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original bicyclane): Isomers	Products (Per cent by weight on original bicyclane): Other Products	References
1	α-Terpinene γ-Terpinene		(622)
1	*d*-1-Isopropyl-4-methylene-5-methylcyclopentene-1 "Terpinene"		(533)
1	*d*-1-Isopropyl-4-methylene-5-methylcyclopentene-1 "Terpinene"		(533)
1	*d*-1-Isopropyl-4-methylene-5-methylcyclopentene-1 "Terpinene"	4-Terpinenyl acetate (30%)	(533)
1	*d*-1-Isopropyl-4-methylene-5-methylcyclopentene-1	*d*-4-Terpinenyl formate	(533)
	No isomers	Camphene unchanged	(12)
	Bicyclic isomer	Diterpene	(201)
1	β-Fenchene γ-Fenchene		(320a)
1	β-Fenchene γ-Fenchene		(320a)
1	*l*-α-Fenchene		(620a)
1	*l*-α-Fenchene *l*-1-Methylsantene	Ethyl isofenchyl ether	(320a)
1	*l*-α-Fenchene (small %) *l*-1-Methylsantene (large %)	Ethyl isofenchyl ether	(320a)
	Allo-ocimene (25%)	β-Pinene	(12)
vapor phase with N_2	Dipentene *l*-Limonene (13% on "Product") Myrcene (about 67% on "Product")	β-Pinene (3% on "product") Fraction, b.p. 48–62° at 20 mm. Hg, after removal of β-pinene (8.5% on "product") Myrcene polymers (mainly α-camphorene) (9.5% on "product")	(217b)
1	*l*-α-Pinene		(466)
1	*l*-α-Pinene (96.1%)		(466)
1	"Terpinene"	"Dipinene"	(610)
1	Camphene		(503)
1	Camphene		(459a)
			(513)
	Camphene α-Pinene		(509)
1	α-Pinene		(506)
1	α-Pinene		(506)
1	Camphene		(505)
1	Camphene		(510)

Table 21. Isomerization of Bicy

Reactants: Bicyclane	Reactants: Catalyst (Per cent by weight on bicyclane+catalyst)	Contact Time (hours)	Temp. (°C.)
β-Pinene	HCl-treated ammonium tungstate Steam-treated ammonium tungstate HNO_3-treated ammonium tungstate HCl-treated sodium tungstate Steam-treated ammonium vanadate Steam-treated ammonium molybdate $CH_3 . CO_2H$-treated sodium tungstate (used individually)		heated
β-Pinene (with some α-Pinene)	Borophosphoric acid (dried pieces) Cu tube used Steam (83.3% of pinenes+steam)		350
β-Pinene	Metaboric acid Titanic acids Simple and complex silicic acids Phosphorous and phosphoric acids Vanadic acids Antimonic acids Molybdic acids Phosphomolybdic acids Tungstic acids Phosphotungstic acids Chromoxalic acids (used individually)		heated
β-Pinene	Metavanadic acid (Total 4.76%)	25	100
β-Pinene	Metaboric acid Titanic acid Simple and complex silicic acids Vanadic acids Acid phosphates $NaHSO_4$ Oxalic acid Phthalic acid Sulfonic acids (used individually)		heated
β-Pinene	Boric acid Titanic acid Silicic acid Vanadic acid Molybdic acid Antimonic acids Tungstic acids Borotungstic acids Silicotungstic acids Silicovanadic acids Borophosphoric acids Phosphostannic acid Phosphotungstic acid Phosphomolybdic acid Arsenomolybdic acid Boracetic acid Aluminoxalic acids Chromoxalic acids Acid phosphotungstates Magnesium acid phosphate Manganese acid phosphate Uranium acid phosphate (used individually)		heated
l-β-Pinene	H_2SO_4 $CH_3 . CO_2H$	1	60

Unsaturated Side-Chains

Ref.	Other Products	
(504)	Camphene	1
	α-Pinene	
(511)	Camphene Tar	1
(502)	Camphene	1
	α-Pinene	
(502)	Camphene	1
(508)	Camphene	1
(514)	Camphene	1
	α-Pinene	

Table 21. Isomerization of Bicyclanes

Reactants: Bicyclane	Reactants: Catalyst (Per cent by weight on bicyclane+catalyst)		Contact Time (hours)	Temp. (°C.)
β-Pinene	Organic acids Neutral solvents, such as toluene, xylene, or α-pinene	 (20–30%)		140–150
l-β-Pinene	Benzoic acid	(47.6%)	30	125
l-β-Pinene	Benzoic acid	(64.5%)	30	125
l-β-Pinene	Benzoic acid	(73.0%)	30	125
l-β-Pinene	Benzoic acid	(50%)	10–20	125–130
l-β-Pinene	Benzoic acid Toluene (solvent)	(30.5%) (52.7%)	30	123
l-β-Pinene	Benzoic acid			below 145
l-β-Pinene	Salicylic acid	(67%)	12–20	160
l-β-Pinene	Abietic acid	(81.8%)	10	130–135
l-β-Pinene	Abietic acid	(81.8%)	20	130–135
l-β-Pinene	Abietic acid	(81.8%)	10	145–150
l-β-Pinene	Abietic acid	(81.8%)	20	145–150
l-β-Pinene	Abietic acid	(81.8%)	10	160–165
l-β-Pinene	Abietic acid	(81.8%)	20	160–165
l-β-Pinene	Abietic acid	(81.8%)	10	175–180
l-β-Pinene	Abietic acid	(81.8%)	20	175–180
l-β-Pinene	Colophony	(75%)	15–20	"160–100"
l-β-Pinene	Trichlorophenol	(74.4%)	30	145
l-β-Pinene	Picric acid Benzene (solvent)	(13.3%) (20%)	0.5	120
β-Pinene	Picric acid			b.p. (?)
l-β-Pinene	Stearin		30	145

with Unsaturated Side-Chains—Continued

Pressure (atms.)	Products (Per cent by weight on original bicyclane) Isomers		Other Products		References
	α-Pinene Other cyclic terpenes		Bornyl esters Isobornyl esters		(18)
1	$\frac{l\text{-Limonene}}{l\text{-}\alpha\text{-Pinene}} = 0.1173$		Bornyl benzoate Isobornyl benzoate Fenchyl benzoate		(21)
1	$\frac{l\text{-Limonene}}{l\text{-}\alpha\text{-Pinene}} = 0.2484$		Bornyl benzoate		(21)
1	$\frac{l\text{-Limonene}}{l\text{-}\alpha\text{-Pinene}} = 0.5030$		Bornyl benzoate		(21)
1	α-Pinene	(86%)	Bornyl benzoate	(14%)	(20)
1	*l*-α-Pinene		Bornyl benzoate		(21)
	α-Pinene				(19)
1	Limonene *l*-α-Pinene "Terpinene"	(50%)	Bornyl esters	(35–36%)	(19)
1	Camphene (?) *l*-α-Pinene	 (1%)			(19)
1	Camphene (?) *l*-α-Pinene	 (17%)			(19)
1	Camphene (?) *l*-α-Pinene	 (23%)			(19)
1	Camphene (?) *l*-α-Pinene	 (49.7%)			(19)
1	Camphene (?) *l*-α-Pinene	 (52%)			(19)
1	Camphene (?) *l*-α-Pinene	 (74.1%)			(19)
1	Camphene (?) *l*-α-Pinene	 (75%)			(19)
1	Camphene (?) *l*-α-Pinene	 (97.6%)			(19)
1	*l*-α-Pinene	(70%)			(20)
1	*l*-α-Pinene	(large %)	Bornyl esters Fenchyl esters	(trace) (trace)	(19)
	l-Camphene *l*-Limonene *l*-α-Pinene		*d*-Bornyl picrate *l*-Bornyl picrate Isobornyl picrate *d*-Fenchyl picrate	(trace)	(133)
1	Camphene Dipentene		Bornyl picrate Diterpene H_2O	 (small amount)	(322)
1	*l*-α-Pinene	(70%)			(20)

Table 22. Isomeriza

Reactants: Tricyclane	Reactants: Catalyst (Per cent by weight on tricyclane+catalyst)		Contact Time (hours)	Temp. (°C.)
Cyclofenchene	Pt-charcoal			300
Cyclofenchene	Activated Florida earth		(short)	b.p.
Cyclofenchene	$KHSO_4$, H_2SO_4, 1.35% in excess of theoretical	(40.0%)	3	b.p.
Cyclofenchene	$KHSO_4$, H_2SO_4, 1.36% in excess of theoretical	(38.5%)	1	b.p.
Cyclofenchene	H_3PO_4, 85%; H_2O, 15%	(31.0%)	5	b.p.
Cyclofenchene	Phthalic anhydride	(37.5%)	3.5	190–200
Tricyclene	Ni			180–200
Tricyclene	$NaHSO_4$			168
Tricyclodecane, m.p. 77° (*i.e.*, Tetrahydro-di-cyclopentadiene)	H_2SO_4, $H_2S_2O_7$		(long)	above 77
Tetradecahydroanthracene (liquid form)	Ni		4	270
Tetradecahydroanthracene (liquid form)	MoS_3	(18.9%)	1 at 330 then 1 at 380	
Tetradecahydroanthracene (liquid form)	$AlCl_3$	(33.3%)	0.25	100
Tetradecahydroanthracene (solid form)			1.50	460
Tetradecahydroanthracene (solid form)	MoS_3		1.50	460
Tetradecahydroanthracene (solid form)	$AlCl_3$	(9.09%)	1.50	100
Tetradecahydroanthracene (solid form)	$AlCl_3$	(9.09%)	3	100
Tetradecahydrophenanthrene	MoS_3	(19.0%)	1	380
Tetradecahydrophenanthrene	$AlCl_3$	(9.09%)	1	100

tion of Tricyclanes

Pressure (atms.)	Products (Per cent by weight on original tricyclane) Isomers	Other Products	References
(CO_2)	α-Fenchene β-Fenchene		(669)
1	1-Methylsantene	Polymers	(587)
1	β-Fenchene (over 37.3%) γ-Fenchene (below 36.9%)		(320)
1	β-Fenchene } γ-Fenchene } ("100%")		(320)
1	1-Methylsantene	Cyclofenchene	(320)
bomb	β-Fenchene (32%) γ-Fenchene (16%)	*dl*-Isofenchyl alcohol *dl*-Isofenchyl acid phthalate	(320)
(N_2)	*dl*-Camphene		(369)
	dl-Camphene		(355)
1	Tricyclodecane, m.p. 9°		(162)
high (H_2)	Tetradecahydroanthracene (solid form) (45%)	Tetradecahydroanthracene (liquid form) (55%)	(637)
98 (H_2)	Tetradecahydroanthracene (solid form) (2.3%)		(451)
1	Tetradecahydroanthracene (solid form) (25%)		(451)
100 (H_2)	Tetradecahydrophenanthrene	Tetradecahydroanthracene (solid form) (22%)	(451)
100 (H_2)	Tetradecahydrophenanthrene		(451)
1	Liquid form of tetradecahydroanthracene (?) Tetradecahydrophenanthrene (?) } (68.9%)	Tetradecahydroanthracene (solid form)	(451)
1	Liquid form of tetradecahydroanthracene (?) Tetradecahydrophenanthrene (?) } (67.5%)		(451)
100 (H_2)	Tetradecahydroanthracene (solid form) (pure, 4.1%) (crude, 94%)		(451)
1	Tetradecahydroanthracene (solid form) (19%) (25% with recycle of filtrate)		(451)

Table 23. Isomerization of Cyclenes and

Reactants: Cyclene	Reactants: Catalyst (Per cent by weight on cyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Methylcyclopropene-1	Al_2O_3		325
Cyclohexene	Al_2O_3 (commercial grade with some SiO_2)	5.5–6 g. feed per 121 cc. catalyst per hour (two passes)	450
Cyclohexene	BeO	5 g. feed per 44.2 cc. catalyst per hour (re - treated the b.p. 73.5–80.5° fraction from the initial product)	450
Cyclohexene	Silica gel	(one pass)	400
Cyclohexene	Silica gel	5.5–6 g. feed per hour (one pass)	450
Cyclohexene	TiO_2	5 g. feed per 88.4 cc. catalyst per hour (re - treated the b.p. 75–83° fraction from the initial product)	350
Cyclohexene	TiO_2	5 g. feed per 88.4 cc. catalyst per hour	400
Cyclohexene	TiO_2	5 g. feed per 88.4 cc. catalyst per hour	450
Cyclohexene	ThO_2, V_2O_3, ZrO_2, or MnO		400–450
Cyclohexene	H_3PO_4 on silica	20 sec.	350
Cyclohexene	H_3PO_4 on silica	20 sec.	400
1-Methylcyclohexene-1	Quinoline-hydriodide Quinoline		heated
4-Methylcyclohexene-1 (1-Methylcyclohexene-3)	Silica gel		450
1-Methyl-4-isopropylcyclohexene-1 (Carvomenthene)	Bleaching earth Pumice Silica gel "Tonsil" Magnesium sulfate Copper phosphate (used individually)		300–450
1-Methyl-4-isopropylcyclohexene-1	Pumice Cu Copper phosphate (used individually)		above 300

Cyclenes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original cyclene) Isomers		Other Products		References
	Butadiene-1,2				(373)
1	"Methylcyclopentene"		Cyclohexene		(665)
1	"Methylcyclopentene"	(48.2%)	Cyclohexene		(12a)
1	"Methylcyclopentene"		Cyclohexene (?) Fraction, b.p. 200–205°		(665)
1	"Methylcyclopentene"	(44.8%)	Cyclohexene		(665)
1	"Methylcyclopentene"	(19%)	Cyclohexene		(12a)
1	"Methylcyclopentene"	(18%)	Cyclohexene		(12a)
1	"Methylcyclopentene"	(11%)	Cyclohexene Benzene		(12a)
1	No isomers		Benzene	(small %)	(12a)
1 (vapor phase)	"Methylcyclopentene"	(below 64%)	Hexane(s) Cyclohexene Polymers	(1.7%?) (below 20%) (15%)	(529a)
1 (vapor phase)	"Methylcyclopentene"	(below 65%)	Hexane(s) Cyclohexene Polymers	(1.7%?) (below 17%) (17%)	(529a)
	Methylenecyclohexane	(2.5%)			(181)
1	"Dimethylcyclopentene"		1-Methylcyclohexene-3		(665)
	1-Isopropyl-4-methylcyclohexene-1 (Menthomenthene)	(50%)			(501)
	1-Isopropyl-4-methylcyclohexene-1				(507)

Table 23. Isomerization of Cyclenes and

Reactants: Cyclene	Reactants: Catalyst (Per cent by weight on cyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Methyl-4-isopropylcyclohexene-1	Superficially-oxidized copper shavings (substantially CuO)		300–350
1-Methyl-4-isopropylcyclohexene-1	Pumice	(one recycle)	450
1-Methyl-4-isopropylcyclohexene-1	Pumice with 5% $MgSO_4$		350
1-Methyl-4-isopropylcyclohexene-1	Granular copper phosphate with 0.5% H_3PO_4		320–350
1-Methyl-4-isopropylcyclohexene-1	Pumice Bricks Silica gel (*i.e.*, activated silicic acid) Bleaching clay Fuller's earth Zeolites "Tonsil" (used individually or mixed with the following:) Copper oxide Copper sulfate Copper phosphate Magnesium oxide Magnesium phosphate Magnesium sulfate		300–450
d-1-Methyl-4-isopropylcyclohexene-2 80% *d*-1-Methyl-4-isopropylcyclohexene-3 20% (This mixture had $\alpha_D = +100.79°$)	*p*-Toluenesulfonic acid C_2H_5OH	(probably less than 4)	100
d-1-Methyl-4-isopropylcyclohexene-2 30% *d*-1-Methyl-4-isopropylcyclohexene-3 70% (This mixture had $\alpha_D = +91.0°$)	*p*-Toluenesulfonic acid C_2H_5OH	2 4 8 (velocity study)	100
d-1-Methyl-4-isopropylcyclohexene-2 (below 30%) *d*-1-Methyl-4-isopropylcyclohexene-3 (above 70%) (This mixture had $\alpha_D = +93.3°$)	*p*-Toluenesulfonic acid (21.8%) C_2H_5OH (34.5%)	18	100
d-1-Methyl-4-isopropylcyclohexene-3	*p*-Toluenesulfonic acid (20%) C_2H_5OH (40%)	24	b.p.
d-1-Methyl-4-isopropylcyclohexene-3	Silica gel	6 g. feed per 106 cc. catalyst per hour (two passes with intermediate fractional distillation)	375 or 400 or 450

Cyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclene): Isomers	Other Products	References
	1-Isopropyl-4-methylcyclohexene-1		(521)
	1-Isopropyl-4-methyl-cyclohexene-1 (87%)		(521)
	1-Isopropyl-4-methyl-cyclohexene-1 (60%)	Recycle stock	(521)
	1-Isopropyl-4-methyl-cyclohexene-1 (50–60%)	Recycle stock	(521)
	1-Isopropyl-4-methyl-cyclohexene-1 (50–90%)	Recycle stock	(521)
1	*dl*-1-Methyl-4-isopropyl-cyclohexene-3 (20%) Shown by optical rotation of product, $\alpha_D = +86.36°$	*d*-1-Methyl-4-isopropyl-cyclohexene-2 (80%)	(258a)
1	*dl*-1-Methyl-4-isopropyl-cyclohexene-3 (70%) Shown by optical rotations of product, $\alpha_D = +30.9°$ after 2 hours $\alpha_D = +28.1°$ after 4 hours $\alpha_D = +27.8°$ after 8 hours	*d*-1-Methyl-4-isopropyl-cyclohexene-2 (30%)	(258a)
1	*dl*-1-Methyl-4-isopropyl-cyclohexene-3 (above 70%) Shown by optical rotation of product, $\alpha_D \doteq +28.3°$	*d*-1-Methyl-4-isopropyl-cyclohexene-2 (below 30%)	(258a)
1	*l*-1-Methyl-4-isopropyl-cyclohexene-3 (27.13%?)	*d*-1-Methyl-4-isopropyl-cyclohexene-3 (72.87%?)	(258)
1	Isomers claimed; product may contain: 1,1-Dimethyl-3-isopropylcyclopentenes, and/or 1,2-Dimethyl-3-isopropylcyclopentenes, and/or 1,3-Dimethyl-3-isopropylcyclopentenes, and/or 1-Ethyl-3-isopropylcyclopentenes, and/or 1-Methyl-3-isobutylcyclopentenes		(666)

Table 24. Isomerization of Cyclenes

Reactants: Cyclene	Reactants: Catalyst (Per cent by weight on cyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Methyl-2-(3-butenyl)-cyclopentene-(1?)	P_2O_5 (9.3%?) H_3PO_4 (sp. gr. 1.75) (81.4%?)	5 (?)	140–150(?)
1-Vinylcyclohexene-3	"Floridin"		200–235
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)		10	200
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)		several	250–270
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)		very long	250–270
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)		5	275–290
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)		6	380
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)		several	380
dl-1-Methyl-4-isopropenylcyclohexene-1 (*dl*-Limonene; Dipentene)	Fuller's earth (28.6%)	1.5	b.p.
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	"Floridin"		210–235
dl-1-Methyl-4-isopropenylcyclohexene-1 (*dl*-Limonene; Dipentene)	Activated clay (prepared from Chasov-Jarsky fire clay No. 5 by 6 hours treatment with 3 times its weight of 10% HCl, washing, and drying at 150–160°) (0.51%)	1	170
dl-1-Methyl-4-isopropenylcyclohexene-1 (*dl*-Limonene; Dipentene)	Activated clay (prepared from Chasov-Jarsky fire clay No. 5 by 6 hours treatment with 3 times its weight of 10% HCl, washing, and drying at 150–160° C.) (first hour) (0.5%) (second hour) (0.99%)	2 (removed the polymers after first hour)	170
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	H_3AsO_4 (20.0%)	0.5	b.p.
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)	H_3PO_4	128	22–32
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	H_3PO_4 on silica		150–250
dl-1-Methyl-4-isopropenylcyclohexene-1 (*dl*-Limonene; Dipentene)	H_2SO_4 C_2H_5OH	1	100
1-Methyl-4-isopropenylcyclohexene-1 (Limonene)	Oxalic acid (anhydrous)	3 (?) at 90–100(?) then 15 (?) at 105–115(?)	
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)	$C_6H_5 . CO_2H$	7	250
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)	Acetone	6	300
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)	Aniline	7	280
d-1-Methyl-4-isopropenylcyclohexene-1 (*d*-Limonene)	H_2O	10	290–360
1-Methyl-4-isopropylidenecyclohexene-1 (Terpinolene)	Acids		heated
1-(3-Butenyl)-cyclohexene-1	P_2O_5 (30%)	3	140

with Unsaturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original cyclene): Isomers	Other Products	References
	3a-Methyl-3a,4,7,7a-tetrahydroindan (89%)	Unchanged hydrocarbon (11%)	(170)
	1-Ethylidenecyclohexene-2		(550)
	dl-Limonene (Dipentene) (trace)	*d*-Limonene (large %) Polymer (trace)	(107)
	dl-Limonene (Dipentene)	Polymers	(615)
	dl-Limonene (Dipentene)		(108)
sealed tube	*dl*-Limonene (Dipentene) (small %)	*d*-Limonene (large %) Polymer (5%)	(107)
	dl-Limonene (Dipentene) (small %)	*d*-Limonene (large %) Polymer (5%)	(107)
	dl-Limonene (Dipentene) (small %)	Polymer	(108)
1	"Terpinene"	"Dipinene"	(610)
	Isolimonene Terpinolene	Polymers	(550)
1	Terpinolene (over 26.3% but less than 40.6%)	Dipentene (over 46.5% but less than 60.8%) Polymers (12.9%)	(480a)
1	α-Terpinene (15.8%) Terpinolene (over 14.83% but less than 23.46%)	Dipentene (over 30%) *p*-Menthene-3 (5.76%) *p*-Cymene (?) Polymers (25.02%)	(480a)
1	"Terpinene"		(208) (209)
1	α-Terpinene (4%) γ-Terpinene	A diterpene (75%)	(103)
1	Two bicyclic isomers	Tricyclic diterpene	(275a)
1	α-Terpinene γ-Terpinene	Resins	(617)
1	α-Terpinene		(394)
	dl-Limonene (trace?)	*d*-Limonene (large %)	(107)
	dl-Limonene (trace?)	*d*-Limonene (large %)	(107)
	dl-Limonene (trace?)	*d*-Limonene (large %)	(107)
	dl-Limonene (Dipentene) (small %)	*d*-Limonene (large %) Polymer (10%)	(107)
1	α-Terpinene γ-Terpinene		(620)
1	1,2,3,4,5,6,7,8-Octahydronaphthalene		(353)

Table 24. Isomerization of Cyclenes

Reactants: Cyclene	Reactants: Catalyst (Per cent by weight on cyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Methyl-2-(3-butenyl)-cyclohexene-1	H_3PO_4		130
Cycloisoprenemyrcene	H . CO_2H, 85% H_2O, 15% (72.4%)	10 at then 2 at	100 120
l-Zingiberene	"50% H_2SO_4" CH_3 . CO_2H	6	60–65
α-Camphorene	H_2SO_4 CH_3 . CO_2H		
α-Camphorene	H . CO_2H, 95% H_2O, 5%	0.5	heated
α-Camphorene	H . CO_2H, 95% H_2O, 5%	3.5	heated
α-Carotene	Al_2O_3 Solvent		room
α-Carotene	Activated Al_2O_3, 50% Inactive Al_2O_3, 50% Light petroleum+benzene (solvent)		room
α-Carotene	MgO Solvent		room
Neo-α-carotene	Al_2O_3 Solvent		room
Pseudo-α-carotene	Solvent (?light petroleum+benzene)	2 months	−2
Pseudo-α-carotene	Solvent (?light petroleum+benzene)	24 hours 2 weeks 2 months (velocity study)	20 20 20
Pseudo-α-carotene	Light petroleum+benzene (solvent)	0.5	80
Pseudo-α-carotene	I_2 (Benzine?)	0.5 1.0 (velocity study)	
Pseudo-α-carotene	Al_2O_3 Solvent		room
β-Carotene	Light petroleum+benzene (equal volumes as solvent) (99.95%)	1 week 2 weeks 4 weeks 12 weeks (velocity study)	−2 −2 −2 −2
β-Carotene	Light petroleum+benzene (equal volumes as solvent) (used 5 ml. per 2.3 mg. β-carotene) Activated Al_2O_3, 33.3% Ordinary Al_2O_3, 66.7% } For simple chromatography	no delay	room
β-Carotene	Light petroleum+benzene (solvent) In the dark	1 day 7 days 18 days 35 days 49 days (velocity study)	20 20 20 20 20
β-Carotene	Solvent (?light petroleum+benzene)	1 3 24 (velocity study)	40 40 40

with Unsaturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclene) Isomers		Other Products		References
	cis-9-Methyl-1,4,5,6,7,8,9,10-octahydronaphthalene				(253)
1	Bicycloisoprenemyrcene	(66.7%)			(484)
1					
1	*l*-Iso-zingiberene				(490) (495) (535)
	Bicyclic isomer				(537)
1	Bicyclic isomer				(494)
1	Tricyclic isomer				(494)
1	Neocarotene				(210)
1	Neocarotene	(30–33%)	α-Carotene		(211)
1	Neocarotene				(210)
1	β-Carotene Neocarotene		Neo-α-carotene		(211)
1 (N_2)	β-Carotene	(5.5%)	Pseudo-α-carotene	(94.5%)	(102)
1	β-Carotene	(5%)	Pseudo-α-carotene	(95%)	(102)
1	β-Carotene	(20%)	Pseudo-α-carotene	(80%)	
1	β-Carotene	(47%)	Pseudo-α-carotene	(53%)	
1	β-Carotene	(68.7%) (equilibrium value)	Pseudo-α-carotene	(31.3%)	(102)
1	β-Carotene	(49%)	Pseudo-α-carotene	(51%)	(661)
1	β-Carotene	(54%)	Pseudo-α-carotene	(46%)	
1	β-Carotene				(210)
1	Pseudo-α-carotene	(below 1.9%)	β-Carotene	(above 98.1%)	(102)
1	Pseudo-α-carotene	(1.7%)	β-Carotene	(98.3%)	
1	Pseudo-α-carotene	(below 3.0%)	β-Carotene	(above 97.0%)	
1	Pseudo-α-carotene	(2.5%)	β-Carotene	(97.5%)	
1	No isomers		β-Carotene unchanged		(102)
1	Pseudo-α-carotene	(below 1%)	β-Carotene	(above 99%)	(102)
1	Pseudo-α-carotene	(5.5%)	β-Carotene	(94.5%)	
1	Pseudo-α-carotene	(6.2%)	β-Carotene	(93.8%)	
1	Pseudo-α-carotene	(10.0%)	β-Carotene	(90.0%)	
1	Pseudo-α-carotene	(11.1%)	β-Carotene	(88.9%)	
1	Pseudo-α-carotene	(4%)	β-Carotene	(96%)	(102)
1	Pseudo-α-carotene	(5.4%)	β-Carotene	(94.6%)	
1	Pseudo-α-carotene	(11.2%)	β-Carotene	(88.8%)	

Table 24. Isomerization of Cyclenes

Reactants			
Cyclene	Catalyst (Per cent by weight on cyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
β-Carotene	Solvent (?light petroleum+benzene)	1 3 (velocity study)	60 60
β-Carotene	Light petroleum (solvent) (used 75 ml. per 30 mg. β-carotene)	2 (evaporated to the point of crystallization)	70–80
β-Carotene	Light petroleum (solvent)	(evaporated to the point of crystallization)	b.p.
β-Carotene	Light petroleum+benzene (equal volumes as solvent) Activated Al_2O_3, 33.3%, Ordinary Al_2O_3, 66.7% For simple chromatography	1 3 (velocity study)	77–80 77–80
β-Carotene	Solvent (?light petroleum+benzene) $Ca(OH)_2$ (For simple chromatography)	(time to reach equilibrium composition)	80
β-Carotene	(Benzine?)	0.5–1.0	80
β-Carotene	I_2 (0.1 mg. per 10 mg. β-carotene) Benzine	1.0	room (?)
β-Carotene	I_2 (Benzine?)	0.5 1.0 (velocity study)	room (?) room (?)
β-Carotene	Al_2O_3 Solvent		room
β-Carotene	Activated Al_2O_3, 25%, Ordinary Al_2O_3, 75% Light petroleum (solvent)	(several passes)	room
β-Carotene	$Ca(OH)_2$ Solvent		room
β-Carotene	$KMnO_4+Na_2CO_3+H_2O$ Benzene (solvent) Later, $Ca(OH)_2$ adsorption	1.5 (oxidation)	room
Neocarotene	Solvent		"crystallization"
1-Ethynylcyclohexene-1	20% Pt+80% charcoal		200–205

with Unsaturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original cyclene) Isomers		Other Products		References
1	Pseudo-α-carotene	(7–8%)	β-Carotene	(92–93%)	(102)
1	Pseudo-α-carotene	(9.1–10.3%)	β-Carotene	(89.7–90.9%)	
1	Pseudo-α-carotene	(33.3%)	β-Carotene	(66.7%)	(102)
1	Pseudo-α-carotene	(27%)	β-Carotene	(73%)	(102)
1	Pseudo-α-carotene	(8–9%)	β-Carotene	(91–92%)	(102)
1	Pseudo-α-carotene	(31%)	β-Carotene	(69%)	
1	Pseudo-α-carotene	(29%)	β-Carotene	(71%)	(102)
1	Pseudo-α-carotene		β-Carotene		(661)
1	Pseudo-α-carotene		β-Carotene		(661)
1	Pseudo-α-carotene	(7%)	β-Carotene	(93%)	(661)
1	Pseudo-α-carotene	(12%)	β-Carotene	(88%)	
1	Pseudo-α-carotene				(210)
1	Pseudo-α-carotene	(40–50%)	Oxidation products	(50–60%)	(210)
1	Pseudo-α-carotene	(below 40%)			(210)
1	Pseudo-α-carotene		β-Apo-4-carotenal β-Carotenal		(296) (297)
1	Neo-α-carotene				(211)
1 (CO_2)	Ethylbenzene	(100%)			(344)

Table 25. Isomerization of Cyclo

Reactants: Cyclodiene	Reactants: Catalyst (Per cent by weight on cyclodiene+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Methyl-4-isopropylcyclohexadiene-1,3 (α-Terpinene)	H_3PO_4	220	room
1-Methyl-4-isopropylcyclohexadiene-1,4 (γ-Terpinene)	Maleic anhydride (Reactant) (42.1%)		heated
l-1-Methyl-4-isopropylcyclohexadiene-1,5 (*l*-α-Phellandrene)	H_3PO_4		room
d-1-Methyl-4-isopropylcyclohexadiene-1,5 (*d*-α-Phellandrene) [Elemi oil]	H_2SO_4 C_2H_5OH	few min.	room
1-Methyl-4-isopropylcyclohexadiene-1,5 (α-Phellandrene)	H_2SO_4 C_2H_5OH	several	b.p.

Table 26. Isomerization of Cyclo

Reactants: Cyclodiene	Reactants: Catalyst (Per cent by weight on cyclodiene+catalyst)	Contact Time (hours)	Temp. (°C.)
1,1-Dimethyl-4-methylenecyclohexadiene-2,5			160
1,1-Dimethyl-4-methylenecyclohexadiene-2,5	HCl (to saturation) $CH_3 . CO_2H$ (solvent)	1	0
1,1,2-Trimethyl-4-methylenecyclohexadiene-2,5	H_2SO_4 $CH_3 . CO_2H$ (solvent)		
1,1-Dimethyl-4-ethylidenecyclohexadiene-2,5	HCl (to saturation) $CH_3 . CO_2H$ (solvent) (68%)	1	0
1,1,3-Trimethyl-4-ethylidenecyclohexadiene-2,5	70% H_2SO_4 (34%) $CH_3 . CO_2H$ (solvent) (45%)		20–40
1,1-Dimethyl-4-propylidenecyclohexadiene-2,5	HCl $CH_3 . CO_2H$ (solvent)		
1,1,2,5-Tetramethyl-4-methylenecyclohexadiene-2,5	HCl $CH_3 . CO_2H$ (solvent)		15–30
1,1,2,6-Tetramethyl-4-methylenecyclohexadiene-2,5	H_2SO_4 $CH_3 . CO_2H$ (solvent)		b.p.
d-1,2-Dimethyl-4-isopropenylcyclohexadiene-2,6	HCl, 2% $CH_3 . CO_2H$, 98% (83.3%)	5	b.p.
d-1-Methyl-2-ethyl-4-isopropenylcyclohexadiene-2,6	HCl, 2% $CH_3 . CO_2H$, 98% (84.0%)	5	b.p.
d-1-Methyl-2-propyl-4-isopropenylcyclohexadiene-2,6	HCl, 3% $CH_3 . CO_2H$, 97% (?%)	4	b.p. (?)
l-β-Curcumene	Inert gases used		380
l-β-Curcumene	Na $C_5H_{11}OH$		
l-β-Curcumene	H_2SO_4, 10% H_2O, 90%	several	100

dienes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original cyclodiene) Isomers		Other Products		References
1	No isomers		α-Terpinene recovered		(103)
1	α-Terpinene (isolated as maleic anhydride adduct) (corresponding yield of free α-terpinene is reported here)	(8.3%)			(206b)
1	α-Terpinene γ-Terpinene	(19.5%)	A diterpene	(40%)	(103)
1	α-Terpinene γ-Terpinene				(619)
1	α-Terpinene γ-Terpinene		Resins		(617)

dienes with Unsaturated Side-Chains.

Pressure (atms.)	Products (Per cent by weight on original cyclodiene) Isomers		Other Products		References
1	1,2,4-Trimethylbenzene (?)		Condensation product		(22)
1	1,2,4-Trimethylbenzene				(23)
1	1,2,3,5-Tetramethylbenzene	(small %)	Polymer	(large %)	(23)
1	1,2-Dimethyl-4-ethylbenzene				(23)
1	1,2,5-Trimethyl-4-ethylbenzene				(23)
1	1,2-Dimethyl-4-propylbenzene				(23)
1	Pentamethylbenzene				(23)
1	Pentamethylbenzene				(23)
1	1,2-Dimethyl-4-isopropylbenzene	(70.0%)			(311)
1	1-Methyl-2-ethyl-4-isopropylbenzene	(63.2%)			(311)
1 (?)	1-Methyl-2-propyl-4-isopropylbenzene	(60.0%)			(310)
(increased)	Isomer				(459)
	Isomer (b.p. 129-130° at 7 mm. Hg)				(459)
1	*l*-Bicyclic isomer (b.p. 115–117° at 7 mm. Hg)				(459)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
d-α-Thujene		over 2 months	room
d-α-Thujene (partially racemized)	HCl (5%) in C_2H_5OH; used 100 cc. of this reagent per 41.7 g. or 50 cc. of the α-thujene	15 min.	b.p.
α-Thujene	Maleic anhydride (Reactant) (42.4%)		heated
α-Thujene	Benzoquinone (Reactant) (23.8%) 0.05*N* HCl (in C_2H_5OH) (61.1%)	2	b.p.
d-α-Pinene		113.5	184.5
d-α-Pinene		115	184.6
d-α-Pinene	"Pyrex" reaction-vessel	12	200
d-α-Pinene	"Pyrex" reaction-vessel	50.5	200
d-α-Pinene	Carius tube used	50	200
d-α-Pinene	Carius tube used	100	200
d-α-Pinene	Carius tube used	200	200
d-α-Pinene		3.6	237
α-Pinene (American turpentine oil)		1	250–270
d-α-Pinene (American turpentine oil)		2	300
l-α-Pinene (French turpentine oil)		2	300
d-α-Pinene	"Pyrex" reaction-vessel	250–275 g. pinene per hour	370–375
d-α-Pinene	(Pumice?)	3.5	420
d-α-Pinene	Petroleum (solvent)	32.8	197.8
d-α-Pinene	Petroleum (solvent)	433 min.	217.9
d-α-Pinene	Acetophenone (solvent)	6	217.5
d-α-Pinene	1-Methylnaphthalene (solvent)	299 min.	218
α-Pinene	Activated Carbon		200

Bicyclenes with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original bicyclene) Isomers		Other Products		References
1	*l*-α-Thujene (small amount)		*d*-α-Thujene (principally)		(546)
1	α-Terpinene (isolated as maleic anhydride adduct) (corresponding yield of free α-terpinene is reported here)	(18.7%)	α-Terpinene monohydrochloride α-Terpinene dihydrochloride		(206b)
	γ-Terpinene	(45%)			
1	*dl*-α-Phellandrene (isolated as maleic anhydride adduct) (corresponding yield of free α-phellandrene is reported here)	(3.1%)	*p*-Cymene	(41%)	(206b)
	α-Terpinene (isolated as maleic anhydride adduct) (corresponding yield of free α-terpinene is reported here)	(15.6%)			
1	α-Terpinene (isolated as benzoquinone adduct) (corresponding yield of free α-terpinene is reported here)	(7.5%)	Quinhydrone		(206b)
vapor phase	Dipentene (*d*+*dl*-α-Pinene reported)		*d*-α-Pinene		(557)
liquid phase	Dipentene (*d*+*dl*-α-Pinene reported)		*d*-α-Pinene		(557)
vapor phase	Dipentene	(10.5%)	*d*-α-Pinene		(112)
vapor phase	Dipentene	(76.3%)	*d*-α-Pinene		(112)
liquid phase	Dipentene	(90%)	*d*-α-Pinene		(112)
liquid phase	Dipentene	(69%)	High-boiling residue	(22%)	(112)
liquid phase	Dipentene	(46%)	High-boiling residue	(50%)	(112)
vapor phase	Dipentene (*d*+*dl*-α-Pinene reported)		*d*-α-Pinene		(557)
	Dipentene		Polymers		(615)
bomb	Dipentene		Polymer		(60)
bomb	Dipentene	(20%)	*l*-α-Pinene		(462)
vapor phase with N_2	Allo-ocimene Dipentene α-Pyronene β-Pyronene	(40% of product) (42% of product) (6% of product) (6% of product)	α-Pinene	(3% of product)	(217a)
vapor phase with N_2	Dipentene		α-Pinene	(50%)	(105)
	Dipentene (*d*+*dl*-α-Pinene reported)		*d*-α-Pinene		(557)
	Dipentene (*d*+*dl*-α-Pinene reported)		*d*-α-Pinene		(557)
	Dipentene (*d*+*dl*-α-Pinene reported)		*d*-α-Pinene		(557)
	Dipentene (*d*+*dl*-α-Pinene reported)		*d*-α-Pinene		(557)
	Dipentene		Cymene $C_{10}H_{18}$ (b.p. 164°)		(202)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
α-Pinene	Activated Carbon Steam			300
α-Pinene	Activated charcoal, Silex, manganese oxide, or kieselguhr			150–200
l-α-Pinene	Activated charcoal	(20%)	1.5	145–150
l-α-Pinene	Activated charcoal B_2O_3 or H_3BO_3			heated
l-α-Pinene	(Activated charcoal?)			heated
α-Pinene	Red phosphorus			100–200 200–300
l-α-Pinene	Al; $HgCl_2$; I_2		20	250
α-Pinene	Cu gauze			300–350
dl-α-Pinene	Cu gauze			350
α-Pinene	Cu gauze		100 g. feed per hour	340
α-Pinene	Reduced Cu			340–350
α-Pinene	Reduced Cu (*via* $CuO+CH_3OH$)		70 g. feed per hour	340–350
α-Pinene	Reduced Cu; or glass			380–390 (?)
d-α-Pinene (French turpentine oil)	Fe			
α-Pinene	Al_2O_3 (*via* ammonium alum+heat)		3.1 g. feed per 10 g. catalyst per minute	410
α-Pinene	Al_2O_3	(4.76%)	10	b.p.
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	50
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	70
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	100
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	8	100
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	2	115
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	115
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	8	115
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	4	125
α-Pinene (Turpentine oil)	Tikhvin bauxite	(40%)	2	150
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	4	10
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	4	20
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	8	20
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 1	(40%)	2	45
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 2	(40%)	2	70

Bicyclic ... Chain with ... (Continued)

Products

% by weight on original ...

Camphene Cymene (202)

$C_{10}H_{16}$ (b.p. 164°)

Dipentene

Dipentene

Limonene (70%)

"Terpinene"

Camphene (3%)

Dipentene p-Cymene

Limonene

Camphene liquid phase (91)

vapor phase (383)

Dipentene l-α-Pinene (206)

Allo-ocimene (144)

Dipentene

α-Pyronene

β-Pyronene

dl-α-Pyronene (145)

β-Pyronene

Allo-ocimene (148)

Limonene

α-Pyronene

β-Pyronene

Allo-ocimene (8)

Allo-ocimene 1 (11)

Allo-ocimene (8)

Dipentene (272)

(H_2)

Dipentene α-Pinene (391)

Low-boiling alkylbenzenes

α-Terpinene

Terpinolene

Camphene 1 (91)

(383)

Camphene Polymers (586)

Dipentene

Camphene Polymers (586)

Dipentene

Camphene Polymers (586)

Dipentene

Camphene Polymers (586)

Camphene Polymers (586)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 2 (40%)	2	100
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 2 (40%)	2	100
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 2 (40%)	2	110
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 2 (40%)	4	110
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 2 (40%)	2	130
α-Pinene (Turpentine oil)	Alapaevsk bauxite No. 2 (40%)	2	150
α-Pinene	Al_2O_3 SiO_2 Kieselguhr Kaolin Clay Fuller's earth Aluminum phosphate Calcium phosphate (used individually)		100–200 200–300
d-α-Pinene (French turpentine oil)	CuO		240
α-Pinene	Copper chromite (Adkins')		300
α-Pinene	Copper chromite (Adkins')		400–410
α-Pinene	Copper chromite (Adkins')		375
α-Pinene	Co-Th catalyst (Fischer and Koch's)		340–400
d-α-Pinene	ThO_2, 25% Pumice, 75%	2.75	390
d-α-Pinene	ThO_2, 25% Pumice, 75%	3.5	420
α-Pinene	"Suprax" glass		340–350
α-Pinene	"Suprax" glass		345–350
α-Pinene	Ordinary soft-glass		350 (?)
α-Pinene	Fuller's earth (28.57%)	4	−20 −5 +25 +158
l-α-Pinene	Fuller's earth (25%)		−20 to over room
l-α-Pinene	"Floridin"		room
α-Pinene (Turpentine oil)	Glukhov kaolin (20%)	2	50–60
α-Pinene (Turpentine oil)	Glukhov kaolin (20%)	2	60–70
α-Pinene (Turpentine oil)	Glukhov kaolin (20%)	4	60
α-Pinene (Turpentine oil)	Glukhov kaolin (20%)	2	70–80
α-Pinene (Turpentine oil)	Glukhov kaolin (20%)	2	90–100
α-Pinene (Turpentine oil)	Glukhov kaolin (20%)	0.25	100
α-Pinene (Turpentine oil)	Bobrik clay (20%)	2	25
α-Pinene (Turpentine oil)	Bobrik clay (20%)	2	50–60
α-Pinene (Turpentine oil)	Bobrik clay (20%)	4	50–60
α-Pinene (Turpentine oil)	Bobrik clay (20%)	2	80–90
α-Pinene (Turpentine oil)	Bobrik clay (20%)	0.20	100
α-Pinene (Turpentine oil)	Cambrian clay (20%)	25 min.	100
α-Pinene (Turpentine oil)	Cambrian clay (20%) (activated by 10% HCl for 6 hrs.)	0.75	45
α-Pinene (Turpentine oil)	Cambrian clay (20%) (activated by 10% HCl for 6 hrs.)	0.50	60

Products

Yield, % by weight on original

Other Products

Polymers (586)
Polymers (586)
Polymers (586)
Polymers (586)
Polymers (586)
Polymers (586)
Camphene liquid phase (91)
vapor phase (383)

Dipentene 110–120 (272)
(H_2)
Allo-ocimene (10)
Allo-ocimene (10)
Dipentene
Unidentified monocyclic, $C_{10}H_{16}$
Allo-ocimene (10)
Dipentene
Allo-ocimene (10)
Dipentene
with N_2 (305)
with N_2 (305)
Dipentene
Allo-ocimene 1 (11)
Allo-ocimene (8)
Allo-ocimene (8)
Dipentene Terpineols (610)
"Terpinene" p-Cymene
α-Pinene
Dipinene
Sesquiterpenes
Polyterpenes
(236)
Dipentene Polyterpenes
Camphene 1 (236)
Polymers (586)
Polymers (586)
Polymers (586)
Polymers (586)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
α-Pinene (Turpentine oil)	Cambrian clay (0.5%) (activated by 10% HCl for 6 hrs.)	0.50	b.p.
α-Pinene (Turpentine oil)	Latny clay "Extra" (20%)	20 min.	100
α-Pinene (Turpentine oil)	Latny clay (20%) (activated by 10% HCl for 6 hrs.)	0.75	45
α-Pinene (Turpentine oil)	Latny clay (20%) (activated by 10% HCl for 6 hrs.)	0.50	60
α-Pinene (Turpentine oil)	Latny clay (0.5%) (activated by 10% HCl for 6 hrs.)	0.50	b.p.
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)	2	80
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)	0.25	100
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)	2	100
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)	4	100
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (20%)	2	120
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Xylene (66.5%)	0.50	b.p.
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Bromobenzene (66.5%)	0.50	160
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Bromobenzene (66.5%)	1.50	160
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Nitrobenzene (66.5%)	0.50	160
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (0.17%) Nitrobenzene (66.5%)	1.50	160
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (20%) (activated by 10% HCl for 6 hrs.)	0.75	45
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (20%) (activated by 10% HCl for 6 hrs.)	0.50	60
α-Pinene (Turpentine oil)	Chasov-Jarsky clay (0.5%) (activated by 10% HCl for 6 hrs.)	0.50	b.p.
d-α-Pinene	Japanese acid clay (40%)	3	10
d-α-Pinene	Japanese acid clay (levigated by HCl, washed by H_2O, dried at 200–250° C.) (11.9%) $CH_3 . CO_2H$ (26.0%) Acetic anhydride (2.6%)	14	25
α-Pinene	Activated clay (0.1 to 1%)	10–30 min.	120
α-Pinene	$MgSO_4 . H_2O$ (4.76%)		b.p.
α-Pinene	$ZnSO_4 . H_2O$ $FeSO_4 . H_2O$ $CoSO_4 . H_2O$ $NiSO_4 . H_2O$ (used individually)		b.p.
α-Pinene	$MgSO_4 . H_2O$ on inactive carriers	50–60 drops feed for 94.25 cc. catalyst per min.	170

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene) Isomers		Other Products		References
1	Camphene	(60%)	Polymers	(9.5%)	(586)
1	Camphene	(56%)	Polymers	(16%)	(586)
1	Camphene	(50%)	Polymers	(16%)	(586)
1	Camphene	(52%)	Polymers	(16%)	(586)
1	Camphene	(62.5%)	Polymers	(10.5%)	(586)
1	Camphene	(below 20%)	Polymers	(8%)	(586)
1	Camphene	(53%)	Polymers	(16%)	(586)
1	Camphene	(50%)	Polymers	(12%)	(586)
1	Camphene	(44%)	Polymers	(21%)	(586)
1	Camphene	(44%)	Polymers	(20%)	(586)
1	Camphene	(40%)	Polymers	(15.0%)	(586)
1	Camphene	(35%)	Polymers	(2.5%)	(586)
1	Camphene	(50%)	Polymers	(10%)	(586)
1	Camphene	(41%)	Polymers	(1.6%)	(586)
1	Camphene	(50%)	Polymers	(6.0%)	(586)
1	Camphene	(52%)	Polymers	(15%)	(586)
1	Camphene	(58%)	Polymers	(12%)	(586)
1	Camphene	(56%)	Polymers	(16%)	(586)
1	*d*-Camphene *d*-Limonene Dipentene	(64%)	Diterpenes	(16%)	(327)
1	*d*-Limonene		Bornyl acetate Isobornyl acetate *d*-α-Terpinyl acetate		(327a)
1	Camphene Terpenes (b.p. 142.5–163°)		Polymers		(349a)
1	Camphene				(459a) (503) (513)
1	Camphene				(503) (513)
vapor phase with N_2	Camphene				(459a) (503) (513)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
α-Pinene (Turpentine oil)	$NiSO_4 . H_2O$		120–130
α-Pinene	$MgSO_4 . H_2O$ $NiSO_4 . H_2O$ (used individually)		heated
α-Pinene	$CaHPO_4$ (total 4.76%)	(long)	140
α-Pinene (Turpentine oil)	Sec. manganese phosphate (1.19%)	(long)	b.p.
α-Pinene	Acid-treated Permutite Acid-treated silica gel (used individually)		90
α-Pinene	HCl-treated ammonium tungstate Steam-treated ammonium tungstate HNO_3-treated ammonium tungstate HCl-treated sodium tungstate Steam-treated ammonium vanadate (used individually)		heated
α-Pinene	HCl-treated ammonium tungstate Steam-treated ammonium tungstate HNO_3-treated ammonium tungstate HCl-treated sodium tungstate Steam-treated ammonium vanadate Steam-treated ammonium molybdate $CH_3 . CO_2H$-treated sodium tungstate (used individually)		heated
α-Pinene	Meta-boric acid Titanic acids Simple and complex silicic acids Phosphorous and phosphoric acids Vanadic acids Antimonic acids Molybdic acids Phosphomolybdic acids Tungstic acids Phosphotungstic acids Chromoxalic acids (used individually)		heated
α-Pinene	Phosphomolybdic acid (total 3.84%)	200	20–30
α-Pinene	Phosphomolybdic acid (total 3.84%)	200	20–30
α-Pinene	Meta-boric acid Titanic acid Simple and complex silicic acids Vanadic acids Acid phosphates $NaHSO_4$ Oxalic acid Phthalic acid Sulfonic acids (used individually)		heated
α-Pinene	Tungstic acid (total 4.76–5.66%)	49.5–59.5	120
α-Pinene	Tungstic acid (total 5.66%)	30–40	130
α-Pinene	Titanic acid (freshly prepared) (0.1%)	20–30	b.p.
α-Pinene	Titanic acid (0.1%)	20–30	b.p.
α-Pinene	Metavanadic acid (total 4.76%)	25	100
α-Pinene	Borophosphoric acid (total 5.66–7.4%)	300–400	120

Products	Tonnage	Ref.
Camphene	1	(503) (513)
Camphene		(509)
Camphene (?)	1	(601a)
Camphene	1	(514) (large %)
Camphene	1	(505)
Camphene	1	(510)
Camphene	1	(504)
Camphene	1	(502)
Camphene	1	(502) (large %)
Camphene (?) "Terpenes"	1	(601a)
Camphene	1	(508)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
α-Pinene	Borophosphoric acid and pumice (compressed into pieces) Cu tube used Steam (80% on α-pinene plus steam)			325
α-Pinene	Boracetic acid	(4.76%)	(long)	100–145
α-Pinene	Boric acid Titanic acid Silicic acid Vanadic acid Molybdic acid Antimonic acids Tungstic acids Borotungstic acids Silicotungstic acids Silicovanadic acids Borophosphoric acids Phosphostannic acid Phosphotungstic acid Phosphomolybdic acid Arsenomolybdic acid Boroacetic acid Aluminoxalic acids Chromoxalic acids Acid phosphotungstates Magnesium acid phosphate Manganese acid phosphate Uranium acid phosphate (used individually)		(long)	heated
l-α-Pinene	H_3AsO_4	(2.44%)	3	b.p.
l-α-Pinene	H_3AsO_4	(1.23%)	3	b.p.
l-α-Pinene	H_3AsO_4	(20.0%)	0.5	b.p.
α-Pinene	Antimonic acid (dried 40 min. at 168–170°)	(total 5–10%)	250–500	50–70
α-Pinene	Antimonic acid	(total 7.4–13.8%)	133–266	60–100
α-Pinene	Antimonic acid	(total 4.76%)	83	120
α-Pinene	Antimonic acid	(total 4.76%)	83	120
α-Pinene	0.442N HCl C_2H_5OH			
α-Pinene	1.379N HCl C_2H_5OH			
α-Pinene (American turpentine oil)	25% HCl C_2H_5OH	(16.67% by volume) (16.67% by volume)	several	100
α-Pinene (American turpentine oil)	HNO_3 (sp. gr. 1.255) C_2H_5OH	(16.67%) (16.67%)		warmed
α-Pinene	1 Normal H_3PO_4			
α-Pinene	3.5 Normal H_3PO_4 C_2H_5OH		5	

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene) Isomers		Other Products		References
1	Camphene	(70–80%)			(511)
1	Camphene		Bornyl acetate	(2%)	(514)
1	Camphene	(to 85%)			(514)
1	Terpinene		*l*-α-Pinene	(large %)	(208)
			Cymene		
			Terpineol		
			H_3AsO_4	(60% recovered)	(209)
			As_2O_3	(0.5%)	
1	Terpinene		α-Pinene		(208)
			Cymene	(small %)	
			Terpineol	(small %)	
1	Terpinene	(over 60%)	Cymene	(below 20%)	(208)
			Terpineol	(1%)	(209)
1	Camphene	(large %)	Terpene alcohols	(small %)	(512)
1	Camphene		Terpene alcohols	(small %)	(514)
1	Camphene	(large %)	Terpene alcohols	(small %)	(502)
1	Camphene		"Other hydrocarbons"	(small %)	(601a)
			Terpene alcohols		
	Camphene		Bornyl chloride		(256)
	Dipentene		Terpineol		
			$C_{10}H_{17}OC_2H_5$		
			Terpin hydrate		
	Dipentene		Bornyl chloride		(256)
			Dipentene hydrochloride		
1	Dipentene	(small %)	Chlorinated products	(large %)	(615)
1	Dipentene				(615)
	No isomers				(255)
	Camphene		Terpineol		(255)
	Dipentene		$C_{10}H_{17}OC_2H_5$		
			$C_{10}H_{16} . H_3PO_4$		

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
α-Pinene	10 Normal H_3PO_4			
α-Pinene	"70% H_3PO_4"	(13.98%)	5	75
d-α-Pinene	H_3PO_4		100	room
l-α-Pinene	H_3PO_4 (sp. gr. 1.7) $CH_3 . CO_2H$	(4.76%?) (63.5%?)		60–70
l-α-Pinene	H_3PO_4 (sp. gr. 1.7) $CH_3 . CO_2H$ Pumice powder	(2.1%) (31%) (1.7%)	0.5	b.p
α-Pinene (Turpentine oil)	"50% H_2SO_4"	(32%)	24	50
α-Pinene (American-d- or French-l-turpentine oil)	Dilute H_2SO_4 (1 : 1 by vol. of H_2O and H_2SO_4)			80
d-α-Pinene	H_2SO_4 H_2O	(33.3%) (20.4%)	6.333	−2
d-α-Pinene	H_2SO_4 H_2O	(35.0%) (16.4%)	6.5	−3
d-α-Pinene	H_2SO_4 H_2O	(35.0%) (16.4%)	5	−8
d-α-Pinene	H_2SO_4 H_2O	(23.6%) (11.1%)	7.5	−3
l-α-Pinene (French turpentine oil)	H_2SO_4	(4.76%)	24	room
α-Pinene	H_2SO_4			
α-Pinene (American turpentine oil)	H_2SO_4	(7.0%)	2–3 days	
α-Pinene (d-American or l-French turpentine oil)	H_2SO_4	(9.7%)		70–130
α-Pinene	0.03N H_2SO_4 C_2H_5OH			
α-Pinene	1.5928N H_2SO_4 C_2H_5OH			
d-α-Pinene	H_2SO_4 C_2H_5OH $HgSO_4$ H_2O	(18.8%) (17.6%) (3.8%) (7.7%)	5	−3
d-α-Pinene	H_2SO_4 C_2H_5OH	(19.5%) (18.3%)	5	−3

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene): Isomers		Other Products		References
	Terpinolene		Cineol		(255)
			Cymene		
1	$\frac{\text{Dipentene}}{\text{Terpinolene}} = 7.08$		Polymerization products		(542)
	α-Terpinene	(11%)	A diterpene	(75%)	(103)
1	*l*-Limonene				(448)
1	*l*-Limonene	(56.3%)			(448)
1	Camphene		Cineol	(0.66%)	(149)
	Dipentene		Cymene		
	Limonene		Four new substances		
	α-Terpinene		Polymers	(67%)	
	γ-Terpinene				
	Terpinolene				
1	"Terpilene," which is dipentene + "terpinene" + terpinolene		Cymene		(14)
			$C_{10}H_{20}$	(small %)	
			Colophony		
1	Dipentene		Borneol		(105)
	Terpinolene	(2.1%)	α-Pinene	(3.8%)	
			Terpineol	(3.8%)	
			Terpin hydrate	(73.9%)	
			Polymer	(6.5%)	
1	Dipentene		Borneol		(105)
	Terpinolene	(2.9%)	Terpineol	(5.1%)	
			Terpin hydrate	(72.4%)	
			Polymer	(6.6%)	
1	Dipentene		Borneol		(105)
	Terpinolene	(4.4%)	α-Pinene	(22.0%)	
			Terpineol	(4.4%)	
			Terpin hydrate	(44.0%)	
			Polymer	(4.6%)	
1	Dipentene		Borneol		(105)
	Terpinolene	(6.0%)	Terpineol	(7.9%)	
			Terpin hydrate	(42.5%)	
			Polymer	(14.7%)	
1	*dl*-Camphene	(10%)	Cymene	(6–8%)	(462)
			Colophony		(464)
	Terpinolene				(616)
					(617)
	α-Terpinene				(617)
	γ-Terpinene				
1	*dl*-Camphene	(20%)	Cymene		(13)
	"Terpilene," which is Dipentene + "Terpinene" + Terpinolene		$C_{10}H_{20}$		(14)
			Polymers		
	Dipentene		$C_{10}H_{17}OC_2H_5$		(254)
	Terpinolene				
	α-Terpinene		Cymene		(254)
	Terpinolene		Cineol		
			Terpin hydrate		
			α-Terpineol		
			$C_{10}H_{17}OC_2H_5$		
1	Dipentene		α-Pinene	(18.4%)	(105)
	Terpinolene	(3.8%)	Terpineol	(32.6%)	
			Terpin hydrate	(1.2%)	
			Polymer	(2.2%)	
1	Dipentene		α-Pinene	(14.7%)	(105)
	Terpinolene	(7.5%)	Terpineol	(28.2%)	

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
d-α-Pinene (*Continued*)	H_2O	(8.0%)		
d-α-Pinene	H_2SO_4	(19.5%)	12	0
	C_2H_5OH	(18.3%)		
	H_2O	(8.0%)		
l-α-Pinene (French turpentine oil)	H_2SO_4 (sp. gr. 1.64)	(16.67%)		100
	C_2H_5OH	(16.67%)		
α-Pinene (American turpentine oil)	H_2SO_4 (sp. gr. 1.64)	(16.67%)	24	100
	C_2H_5OH	(16.67%)		
α-Pinene+β-Pinene (Russian turpentine oil)	H_2SO_4 (sp. gr. 1.64)	(16.67%)	several days	100
	C_2H_5OH	(16.67%)		
d-α-Pinene	H_2SO_4	(20.3%)	5.5	−5
	C_2H_5OH	(19.1%)		
	H_2O	(4.1%)		
d-α-Pinene	H_2SO_4	(17.7%)	6	−4
	C_2H_5OH	(33.2%)		
d-α-Pinene	H_2SO_4	(21.2%)	1.5 at then 0.5 at then 1.0 at	0 / 20 / 65–70
	C_2H_5OH	(19.9%)		
d-α-Pinene	H_2SO_4	(21.2%)	3	−10
	C_2H_5OH	(19.9%)		
d-α-Pinene	H_2SO_4	(21.2%)	9.25	−8
	C_2H_5OH	(19.9%)		
d-α-Pinene	H_2SO_4	(21.2%)	4	0
	C_2H_5OH	(19.9%)		
d-α-Pinene	$H.CO_2H$	(25.3%)	2 months plus 6 days	room
l-α-Pinene (French turpentine oil)	$H.CO_2H$	(33.7%)	26 days	room
d-α-Pinene (American turpentine oil)	$H.CO_2H$	(33.3%)	67 days	room
l-α-Pinene	$H.CO_2H$	(37.4%)	2 years (?)	room
	H_2O	(7.3%)		
l-α-Pinene	$H.CO_2H$	(23.0%)	2 years (?)	room
	H_2O	(9.0%)		
l-α-Pinene	$H.CO_2H$	(19.5%)	2 years (?)	room
	H_2O	(22.9%)		
l-α-Pinene	$H.CO_2H$	(16.8%)	2 years (?)	room
	H_2O	(33.2%)		

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene) Isomers		Other Products		References
			Terpin hydrate Polymer	(1.6%) (1.8%)	
1	Dipentene Terpinolene	(9.9%)	Terpineol Terpin hydrate Polymer	(29.9%) (7.1%) (5.1%)	(105)
1	Dipentene				(191)
1	α-Terpinene γ-Terpinene		Cymene		(615) (616)
1	γ-Terpinene Terpinolene				(669a)
1	Dipentene Terpinolene	(21.1%)	α-Pinene Terpineol Terpin hydrate Polymer	(12.9%) (18.2%) (1.5%) (2.1%)	(105)
1	Terpinolene	(6.8%)	α-Pinene Terpineol Polymer	(49.3%) (2.2%) (11.8%)	(105)
1	Terpinolene	(17.6%)	Polymer	(54.8%)	(105)
1	Terpinolene	(22.0%)	α-Pinene Terpineol Polymer	(17.6%) (5.9%) (4.8%)	(105)
1	Terpinolene	(24.5%)	α-Pinene Terpineol Terpin hydrate Polymer	(9.2%) (6.3%) (1.5%) (9.6%)	(105)
1	Terpinolene	(25.2%)	Terpineol Polymer	(2.94%) (7.35%)	(105)
1	*d*-Camphene *d*-Limonene } Dipentene } α-Terpinene } Terpinolene	 (14.7%) (1.84%)	$H\cdot CO_2H$ *d*-α-Pinene *d*-Diterpilene Bornyl formate } *d*-4-Terpinenyl formate } *d*-4-Terpinenyl formate } *d*-α-Terpinyl formate }	(recovered 41.3%) (below 17%) (10%) (8.1%) (51.5%) 	(460)
1	*l*-Limonene		*l*-α-Pinene Cymene *l*-Diterpilene α-Terpinyl formate Bornyl formate (?)	(13.4%) (large %) 	(328)
1	*d*-Limonene		*d*-α-Pinene Cymene *l*-Diterpilene *d*-α-Terpinyl formate		(328)
sealed tube	Dipentene	(small %)	Diterpilene *l*-Bornyl formate	(large %) (trace)	(78)
sealed tube	*l*-Limonene		Terpin hydrate α-Terpinyl formate	(large %)	(78)
sealed tube	*l*-Limonene		*l*-α-Pinene Terpin hydrate *l*-α-Terpinyl formate	 (3.7%) 	(78)
sealed tube	*l*-Limonene		*l*-α-Pinene Terpin hydrate *l*-α-Terpinyl formate	 (2.6%) (7.3%)	(78)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
l-α-Pinene (French turpentine oil)	$CH_3 . CO_2H$	(71%)	0.5 year	room
d-α-Pinene (American turpentine oil)	$CH_3 . CO_2H$			100
l-α-Pinene (French turpentine oil)	$CH_3 . CO_2H$	(67.0%)	64 at then 2 months at	100 room
l-α-Pinene (French turpentine oil)	$CH_3 . CO_2H$	(30.6%)	5	200
l-α-Pinene	$CH_3 . CO_2H$ $ZnCl_2$	(62.0%) (6.9%)	"overnight"	room
l-α-Pinene	$CH_3 . CO_2H$ H_2O	(45.2%) (3.4%)	3 years	room
l-α-Pinene	$CH_3 . CO_2H$ H_2O	(28.0%) (8.4%)	3 years	room
l-α-Pinene	$CH_3 . CO_2H$ H_2O	(25.8%) (15.5%)	3 years	room
l-α-Pinene (French turpentine oil)	$CH_3 . CO_2H$ 50% Soln. of $C_6H_5 . SO_3H$ Acetic anhydride to remove H_2O	(below 50%)	1.5–2	76
d-α-Pinene	$ClCH_2 . CO_2H$	(20.0%)	35	140–142
d-α-Pinene	$ClCH_2 . CO_2H$ (1 mole per 3 moles α-pinene) Boracetic anhydride $CH_3 . CO_2H$ (solvent)		25	100
d-α-Pinene	$Cl_2CH . CO_2H$	(33.3%)	0.5	90
d-α-Pinene	Oxalic acid (anhydrous) Tetrachloroethane (solvent)	(7.14%) (35.7%)	4	140
l-α-Pinene (?) + *l*-β-Pinene (?) (Turpentine oil, b.p. 158–161°)	Oxalic acid (anhydrous)	(20%)	3 at then 15 at	90–100 105–115
α-Pinene	$C_6H_5 . CO_2H$	(50%)	10–20	125–130

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene): Isomers		Other Products		References
sealed tube	*l*-Limonene		*l*-α-Pinene *l*-Bornyl acetate (*Ld*)-Fenchyl acetate *l*-α-Terpinyl acetate		(74)
1	*d*-Limonene		*d*-α-Pinene *d*-Bornyl acetate *l*-Bornyl acetate *d*-α-Terpinyl acetate		(328)
1 1	*l*-Camphene *l*-Limonene		*l*-α-Pinene *l*-Bornyl acetate (*Ld*)-Fenchyl acetate α-Terpinyl acetate		(75)
autoclave	"Camphene" *l*-Limonene (or else dipentene)	(10–15%) (30–40%)	"Bornyl acetate"	(30–40%)	(662)
1	*l*-Limonene		α-Pinene *l*-α-Terpinyl acetate $C_{10}H_{17}Cl$ (m.p. 47–109°)		(171)
sealed tube (CO_2)	*l*-Limonene		α-Pinene Terpin hydrate α-Terpinyl acetate	 (0.07%)	(78)
sealed tube (CO_2)	*l*-Limonene		α-Pinene Terpin hydrate α-Terpinyl acetate	 (trace)	(78)
sealed tube (CO_2)	*l*-Limonene		α-Pinene α-Terpinyl acetate		(78)
1	Camphene		*l*-α-Pinene Bornyl acetate Isobornyl acetate (*Ld*)-Fenchyl acetate *l*-α-Terpinyl acetate $C_{10}H_{18}$ (b.p. 157–160°)		(35) (36)
1	Camphene *d*-δ-Fenchene (?) *d*-Limonene+dipentene Terpinolene	(11.4%) (3.35%) (42.2%) (8.71%)	*d*-α-Pinene *d*-Borneol Isoborneol *l*-Fenchyl alcohol *d*-Bornyl chloracetate Isobornyl chloracetate *l*-Fenchyl chloracetate $ClCH_2 . CO_2H$ (16% unreacted) H_2O	(1.34%) } (53%) (trace)	(133a)
1	*d*+*dl*-Camphenes *d*-Limonene+dipentene Terpinolene		Bornyl chloracetate Isobornyl chloracetate Fenchyl chloracetate	} (51%)	(133a)
1	*d*-Limonene α-Terpinene		*d*-α-Pinene *d*-Bornyl dichloracetate Isobornyl dichloracetate Fenchyl dichloracetate $Cl_2CH . CO_2H$ (10% unreacted)	 } (90.8%)	(133a)
1	Camphene *d*-Limonene		*d*-α-Pinene *d*-Dibornyl oxalate Diisobornyl oxalate Difenchyl oxalate Tetrachloroethane	 } (26.6%) (8.65%)	(133a)
1	Dipentene α-Terpinene		*dl*-Bornyl ester	(over 15%)	(394)
1	Limonene	(trace)	α-Pinene Bornyl benzoate	(90%) (3–5%)	(20)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Catalyst (Per cent by weight on bicyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
l-α-Pinene (French turpentine oil)	$C_6H_5 . CO_2H$ Cu vessel	(50%)	50	b.p.
d-α-Pinene	Salicylic acid	(27.8%)	60	130–135
d-α-Pinene	Salicylic acid	(33.3%)	50	130–135
d-α-Pinene	Salicylic acid	(50.0%)	50	130–135
d-α-Pinene	*o*-Benzoylbenzoic acid	(33.3%)	50	140
l-α-Pinene	Acetic anhydride B_2O_3	(28.4%) (16.3%)	14	90–95
α-Pinene	Acetic anhydride B_2O_3 $CH_3 . CO_2H$	(7.2–10.3%) (0.68–1.3%) (36.3–43.2%)	15–28	110–120
l-α-Pinene	Acetic anhydride H_3BO_3	(27.5–46.1%) (6.9–16.4%)	17–45	110–130
α-Pinene	Colophony	(66.7%)	6–7	163–165
l-α-Pinene (French turpentine oil)	C_6H_5OH	(25.7%)	5	160
l-α-Pinene (French turpentine oil)	C_6H_5OH	(40.8%)	5	160
l-α-Pinene (French turpentine oil)	C_6H_5OH	(58.0%)	5	160
l-α-Pinene (French turpentine oil)	*o*-Cresol	(16.6%)	5	160
l-α-Pinene (French turpentine oil)	Resorcinol Neutral solvent		5	140
l-α-Pinene (French turpentine oil)	Methyl salicylate	(18.3%)	4	240
l-α-Pinene (French turpentine oil)	*p*-Nitrophenol			b.p. (?)
l-α-Pinene (French turpentine oil)	*p*-Nitro-*m*-cresol		1	b.p.
l-α-Pinene (French turpentine oil)	*m*-Dinitrophenol			b.p. (?)

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene): Isomers		Other Products		References
1	*l*-Camphene	(10%)	*l*-Bornyl benzoate		(76)
	l-Limonene	(33.3%)	(*Ld*)-Fenchyl benzoate	(50%)	
			Colophony		
1	*d*-Limonene	(51.7%)	*d*-α-Pinene	(8.3%)	(133a)
	l-Limonene	(trace)	*d*-Bornyl salicylate		
			Isobornyl salicylate	(49%)	
			Fenchyl s licylate		
			Salicylic acid	(19% unreacted)	
1	*d*-Limonene		*d*-α-Pinene		(133a)
	l-Limonene	(trace)	*d*-Bornyl s licylate		
			Isobornyl salicylate		
			Fenchyl salicylate		
			Salicylic acid	(23% unreacted)	
1	Camphene		*d*-Bornyl salicylate		(133a)
	Dipentene		Isobornyl salicylate	(68%)	
	Terpinolene		Fenchyl salicylate		
			Salicylic acid	(56% unreacted)	
			H_2O	(trace)	
			CO_2	(trace)	
1	Camphene		*d*-α-Pinene		(133a)
	d-Limonene		*d*-Bornyl *o*-benzoylbenzoate		
			Isobornyl *o*-benzoylbenzoate	(48.3%)	
			Fenchyl *o*-benzoylbenzoate		
			o-Benzoylbenzoic acid	(30% unreacted)	
1	*l*-Camphene		*l*-α-Pinene		(268)
	Dipentene		Bornyl acetate		
			Isobornyl acetate		
			Fenchyl acetate		
1	Camphene		α-Pinene		(269)
	Dipentene		*p*-Cymene		
	α-Terpinene		Bornyl acetate		
	Terpinolene		Isobornyl acetate		
			α-Fenchyl acetate (?)		
			β-Fenchyl acetate (?)		
1	*l*-Camphene		*l*-α-Pinene		(268)
	Dipentene		*p*-Cymene		
			Bornyl acetate		
			Isobornyl acetate		
			α-Fenchyl acetate		
			β-Fenchyl acetate		
			α-Terpinyl acetate (?)		
			A diterpene acetate (?)		
1	Camphene				(439)
1	*l*-Camphene		*l*-α-Pinene		(322)
			Phenol		
1	*l*-Camphene		*l*-α-Pinene		(322)
			Phenol		
1	*l*-Camphene		*l*-α-Pinene		(322)
			Phenol		
1	*l*-Camphene		*l*-α-Pinene		(322)
1	*l*-Camphene		*l*-α-Pinene		(322)
4	*l*-Camphene		*l*-α-Pinene		(322)
1	Camphene	(small %)	Diterpene	(trace)	(322)
1	Camphene		Diterpene		(322)
			p-Nitro-*m*-cresol		
1	Camphene		Diterpene		(322)

Table 27. Isomerization of Bicyclenes and

Reactants: Bicyclene	Reactants: Catalyst (Per cent by weight on bicyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
l-α-Pinene (French turpentine oil)	Dinitro-*o*-cresol		b.p. (?)
l-α-Pinene (French turpentine oil)	2,6-Dinitro-*p*-cresol		b.p. (?)
l-α-Pinene (French turpentine oil)	Picric acid (20.0%)		135-b.p.
d-α-Pinene	Picric acid (13.3%) Benzene (solvent) (20%)	0.5	120
l-α-Pinene (French turpentine oil)	Picric acid Toluene (solvent)	1	130–140
l-α-Pinene (French turpentine oil)	2,4,5-Trinitro-*m*-cresol (18–21%) Toluene (solvent) (7–15%)		109
l-α-Pinene (French turpentine oil)	2,4,5-Trinitro-*m*-cresol		b.p. (?)
l-α-Pinene (French turpentine oil)	Trinitrothymol		b.p. (?)
l-α-Pinene (French turpentine oil)	Tribromophenol With or without toluene as solvent	1–50	120–240
l-α-Pinene (French turpentine oil)	Trichlorophenol (6.75%)		b.p. (?)
l-α-Pinene (French turpentine oil)	Trichlorophenol Toluene (solvent)		b.p. (?)
d-Δ^3-Carene	"Suprax" glass		400
d-Δ^4-Carene		4	280
d-Δ^4-Carene	$CH_3 . CO_2H$		b.p.
trans-1,2,3,4,4a,5,8,8a-Octahydronaphthalene (*trans*-Δ^2-Octalin)	P_2O_5	3	140

Bicyclenes with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original bicyclene) Isomers		Other Products		References
1	Camphene		Diterpene		(322)
1	Camphene		Diterpene		(322)
1	*l*-Camphene	(60%)	*l*-α-Pinene	(18.4%)	(322)
	Dipentene	(9.2%)	Diterpene	(3.7%)	
			Bornyl picrate, Picric acid	(30%)	
			Borneol	(trace)	
			H_2O	(trace)	
1	*d*-Limonene		*d*-Bornyl picrate	(24%)	(133)
	d-Camphene		*l*-Bornyl picrate	(trace)	
	d-α-Pinene		Isobornyl picrate	(trace)	
			l-Fenchyl picrate		
1	Camphene	(large %)	*l*-α-Pinene	(trace)	(322)
	Dipentene	(small %)	Bornyl picrate	(trace)	
			H_2O	(trace)	
1	*l*-Camphene		*l*-α-Pinene		(322)
	Dipentene	(trace)	2,4,5-Trinitro-*m*-cresol		
			Bornyl-2,4,5-trinitro-*m*-cresolate	(10–15%)	
1	Camphene		Diterpene		(322)
	Dipentene		Bornyl-2,4,5-trinitro-*m*-cresolate		
1	Camphene		Diterpene		(322)
	Dipentene		Bornyl-trinitrothymolate		
1–4	Camphene	(21% max.)	Diterpene	(trace)	(322)
			Bornyl-tribromophenolate (?)		
1	Camphene		Diterpene		(322)
			Bornyl-trichlorophenolate (?)		
1	Camphene		Diterpene		(322)
			Bornyl-trichlorophenolate (?)		
	No isomers		*d*-Δ^3-Carene unchanged		(12)
	Sylvestrene				(538)
	α-Terpinene				
1	α-Terpinene				(538)
1	1,2,3,4,5,6,7,8-Octahydronaphthalene				(353)

Table 28. Isomerization of Bicyclenes

Reactants: Bicyclene	Catalyst (Per cent by weight on bicyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
Caryophyllene (b.p. 123–124° at 16 mm. Hg)	H_2SO_4 $(C_2H_5)_2O$ Later, NaOH solution	(28%) (21%)	10 at then "overnight" at then alkali at	0–10 room 0
Caryophyllene	H_2SO_4 $CH_3 . CO_2H$			100 (?)
Caryophyllene	H_2SO_4, 1.89% H_2O, 3.77% $CH_3 . CO_2H$, 94.34%	(77%?)	12 (?)	100 (?)
β-Caryophyllene	$H . CO_2H$	(50% by vol.)	several days	b.p.
d-α-Selinene	H_2SO_4 C_2H_5OH	(9.8%) (77.2%)	several	b.p.
Sclarene	$H . CO_2H$	(72.2%)	4	120

Table 29. Isomerization of Bicyclodienes

Reactants: Bicyclodiene	Catalyst (Per cent by weight on bicyclodiene+catalyst)		Contact Time (hours)	Temp. (°C.)
l-Cadinene (regenerated)			12 (?)	330
l-Cadinene	Dilute H_2SO_4		several	heated
Cadinene	H_2SO_4, 57% H_2O, 43%	(98.8%)	36	b.p.
l-Cadinene (regenerated)	"30% H_2SO_4" $CH_3 . CO_2H$	(4.4%) (93.8%)	8	100
l-Cadinene (regenerated)	$CH_3 . CO_2H$	(25%)	24	230–235°

Table 30. Isomerization of Tricyclenes and

Reactants: Tricyclene	Catalyst (Per cent by weight on tricyclene+catalyst)		Contact Time (hours)	Temp. (°C.)
$\Delta^{11,12}$-Dodecahydrophenanthrene				b.p.
Cedrene	$H . CO_2H$	(50% by ? vol.)	several days (?)	b.p.
l-α-Gurjunene (l-Tricyclene-gurjunene)			12	330
l-α-Gurjunene	H_2SO_4 $CH_3 . CO_2H$	(6.9%) (58.7%)	2	100
d-β-Gurjunene (d-Tricyclo-gurjunene)	HCl (gas) $CH_3 . CO_2H$	 (67.7%)		room
l-Sesquichamene	H_2SO_4 C_2H_5OH	(14.3%) (14.3%)	1.5	40–50

with Unsaturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original bicyclene): Isomers		Other Products		References
1	Clovene	(8.5%)	α-Iso-caryophyllene alcohol	(2%)	(488)
1			β-Iso-caryophyllene alcohol	(25%)	
1					
1 (?)	*l*-Isomer (b.p. 126–127° at 24 mm. Hg)		"Caryophyllene alcohol"		(136)
1 (?)	*l*-Isomer (b.p. 126–127° at 24 mm. Hg) *l*-Isomer (b.p. 126–130° at 18 mm. Hg) ("Clovene")		"Isocaryophyllene alcohol"		(137)
1	Clovene		Caryophyllene Formate of "caryophyllene alcohol"	(35%)	(469)
1	*d*-δ-Selinene (?) *d*-ε-Selinene (?)				(492)
1	Tricyclic isomer	(42%)	Sclarene		(489)

with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original bicyclodiene): Isomers	Other Products	References
bomb	*l*-Monocyclic isomer	Cadinene	(536)
	Isomer		(633)
1	Isomer (b.p. 140–145° at 12 mm. Hg)		(493)
1	Isocadinene		(246)
bomb	Isocadinene		(246)

Tricyclenes with Saturated Side-Chains

Pressure atms.	Products (Per cent by weight on original tricyclene): Isomers		Other Products	References
10–26 mm. Hg	$\Delta^{12,13}$-Dodecahydro-phenanthrene		Octahydrophenanthrene Tetradecahydrophenanthrene	(150)
1	Tricyclic isomer	(50%)	Cedrene "Alcoholic substances"	(469)
bomb	*dl*-α-Gurjunene		$C_{10}H_{16}$ $C_{20}H_{32}$	(536)
1	*l*-Iso-α-gurjunene		Polymers	(591)
1	*l*-Iso-β-gurjunene			(591)
1	*l*-Isosesquichamene			(294)

Table 31. Isomerization of Tricyclenes

Reactants: Tricyclene	Reactants: Catalyst (Per cent by weight on tricyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
d-Rimuene		(heating and cooling period)	b.p.
d-Rimuene	$H \cdot CO_2H$, 90% } H_2O, 10% }	48	

Table 32. Isomeriza

Reactants: Tetracyclene	Reactants: Catalyst (Per cent by weight on tetracyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
d-2,4-Cholestadiene	Conc. HCl (2%) "95% C_2H_5OH" (96%)	6–26	b.p.
d-4,6-Cholestadiene	$CHCl_3$ (solvent) (91.1%) HCl (gas) (to saturation)	3	0
Phyllocladene (Dacrene)	SiO_2 tube		800–900
Phyllocladene (Dacrene)	HNO_3 Light petroleum (diluent)		room
Phyllocladene	H_2SO_4, 10% } C_2H_5OH, 90% }		b.p.
Phyllocladene	H_2SO_4, 10% } C_2H_5OH, 90% }		b.p.
d-Phyllocladene (*d*-Sciadopitene)	H_2SO_4 C_2H_5OH	5	b.p.
Phyllocladene	H_2SO_4, 10% } C_2H_5OH, 90% }	few minutes	100
Phyllocladene (Dacrene)	$K_2Cr_2O_7$ $CH_3 \cdot CO_2H$		
Phyllocladene (Dacrene)	$H \cdot CO_2H$, 90% } H_2O, 10% }	"short time"	b.p.
Phyllocladene (Dacrene)	$CH_3 \cdot CO_2H$	"short time"	b.p.

Table 33. Isomeriza

Reactants: Pentacyclene	Reactants: Catalyst (Per cent by weight on pentacyclene+catalyst)	Contact Time (hours)	Temp. (°C.)
d-17,18-*cis*-$\Delta^{12,13}$ (?) -Oleanene	$CH_3 \cdot CO_2H$ (65.6%?) Amalgamated zinc wool (15.6%?) Hydrochloric acid (18.6%?)	6	b.p.
d-17,18-*trans*-$\Delta^{12,13}$ (?) -Oleanene	$CH_3 \cdot CO_2H$ (65.6%) Amalgamated zinc wool (15.6%) Hydrochloric acid (18.6%)	4	b.p.

...with Unsaturated Side-Chains

Products		
Yield (% by weight on original) Isomer	Other Products	
Rimuene (?)		(307)
Phyllocladene	1	(40)

...tion of Tetracyclenes

Products		
Yield (% by weight on original) Pressure Isomer	Other Products	
l-3,5-Cholestadiene		(565)
...Cholestadiene		(150a)
Isophyllocladene	1	(66)
Isophyllocladene (Isodacrene)	1	(66)
Isophyllocladene	1	(87)
Isophyllocladene	1	(90a)
d-Isophyllocladene (d-Isosciadopitene)		(400)
Isophyllocladene	1	(90)
Isophyllocladene (Isodacrene)	1	(66)
Isophyllocladene (Isodacrene)	1	(66)
Isophyllocladene (Isodacrene)	1	(66)

...tion of Pentacyclenes

Products	
Yield (% by weight on original) Isomer	Other Products

Table 35. Isomerization of Benzenes

Reactants: Substituted Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
Toluene	Ultraviolet light (?)			67
1,2-Dimethylbenzene (*o*-Xylene)	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	700
1,2-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	730
1,2-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	750
1,2-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	770
1,2-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	5	50
1,2-Dimethylbenzene	$AlCl_3$ HCl (gas)	(56%)	10 min.	55
1,2-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	0.25	94
1,2-Dimethylbenzene	$AlCl_3$	(16.7%)	6	100
1,3-Dimethylbenzene (*m*-Xylene)	Quartz tube used		15 ml. feed per 219.3 ml. zone per hour	800
1,3-Dimethylbenzene	$AlCl_3$			
1,3-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	0.5	50
1,3-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	1.5	50
1,3-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	5	50
1,3-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	18	50
1,3-Dimethylbenzene	$AlCl_3$ $FeCl_3$ HCl	(26.3%) (32%)	20	50
1,3-Dimethylbenzene	$AlCl_3$ $FeCl_3$ HCl	(55%) (2%)	20	50

with Saturated Side-Chains

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers		Other Products		References
	1-Methylenecyclohexadiene-3,5		Toluene		(376)
1	1,3-Dimethylbenzene	(4.0%)	Gas	(2.1%)	(139)
	1,4-Dimethylbenzene	(trace)	Toluene	(4.6%)	
			1,2-Dimethylbenzene	(76.3%)	
			Condensed products	(12.1%)	
1	1,3-Dimethylbenzene	(6.5%)	Gas	(4.3%)	(139)
	1,4-Dimethylbenzene	(1.4%)	Toluene	(8.2%)	
			1,2-Dimethylbenzene	(59.9%)	
			Condensed products	(3.6%)	
1	1,3-Dimethylbenzene	(10.9%)	Gas	(8.9%)	(139)
	1,4-Dimethylbenzene	(3.5%)	Toluene	(11.5%)	
			1,2-Dimethylbenzene	(38.7%)	
			Condensed products	(24.8%)	
1	1,3-Dimethylbenzene	(16.8%)	Gas	(14.8%)	(139)
	1,4-Dimethylbenzene	(4.6%)	Toluene	(2.8%)	
			1,2-Dimethylbenzene	(22.5%)	
			Condensed products	(25.4%)	
1	1,3-Dimethylbenzene	(below 51.7%)	1,2-Dimethylbenzene	(below 37.6%)	(415)
	1,4-Dimethylbenzene	(below 4.7%)			
1	1,3-Dimethylbenzene	(18.7%)	1,2-Dimethylbenzene	(81.6%)	(414)
1	1,3-Dimethylbenzene	(below 38.6%)	1,2-Dimethylbenzene	(below 31.9%)	(415)
	1,4-Dimethylbenzene	(below 13.4%)			
1	1,2-Dimethylbenzene, 1,3-Dimethylbenzene (mainly), 1,4-Dimethylbenzene	(84%)	Benzene (?)	(2%)	(245)
			Pseudocumene (mainly), Mesitylene	(5%)	
			Tar		
1	No 1,4-dimethylbenzene found		Benzene	(1.5%)	(28)
			Toluene	(22.1%)	
			Xylene of b.p. 135°	(23.5%)	
			Naphthalene, anthracene, and other residues	(17.6%)	
	1,4-Dimethylbenzene		Benzene		(7)
			Toluene		
			Mesitylene		
			Pseudocumene		
			Durene		
			Isodurene		
1	1,4-Dimethylbenzene	(2.8%)	1,3-Dimethylbenzene	(89.2%?)	(415)
1	1,2-Dimethylbenzene	(15%)	1,3-Dimethylbenzene	(72.4%)	(415)
	1,4-Dimethylbenzene	(6.6%)			
1	1,2-Dimethylbenzene	(11.7%)	1,3-Dimethylbenzene	(61.9%)	(415)
	1,4-Dimethylbenzene	(10%)			
1	1,2-Dimethylbenzene	(12.9%)	1,3-Dimethylbenzene	(55.7%)	(415)
	1,4-Dimethylbenzene	(12.1%)			
1	1,2-Dimethylbenzene	(below 17%)	1,3-Dimethylbenzene	(below 68%)	(415)
	1,4-Dimethylbenzene	(below 15%)			
1	1,2-Dimethylbenzene	(below 16%)	1,3-Dimethylbenzene	(below 69%)	(415)
	1,4-Dimethylbenzene	(below 15%)			

Table 35. Isomerization of Benzenes

Reactants: Substituted Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1,3-Dimethylbenzene	$AlCl_3$ HCl	(55.7%)	20	50
1,3-Dimethylbenzene	$AlCl_3$ HCl	(55.7%)	30	50
1,3-Dimethylbenzene	$AlCl_3$ HCl	(1.24%)	48	50
1,3-Dimethylbenzene	$AlCl_3$ HCl	(20.1%)	48	50
1,3-Dimethylbenzene	$AlCl_3$ HCl	(55.7%)	48	50
1,3-Dimethylbenzene	$AlCl_3$	(55.7%)	50	50
1,3-Dimethylbenzene	$AlCl_3$ HCl	(55.7%)	50	50
1,3-Dimethylbenzene	$AlCl_3$ HCl	(55.7%)	75	50
1,3-Dimethylbenzene	$AlCl_3$ HCl	(55.7%)	0.25	94
1,3-Dimethylbenzene	$AlCl_3$ HCl (gas)		6	100
1,3-Dimethylbenzene	$AlCl_3$	(20–25%)		b.p.
1,4-Dimethylbenzene (*p*-Xylene)	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	700
1,4-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	730
1,4-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	750
1,4-Dimethylbenzene	Porcelain tube used		2 g. feed per 353.4 ml. zone per minute	770
1,4-Dimethylbenzene	Quartz tube used		15 ml. feed per 219.3 ml. zone per hour	800

with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers	Other Products	References
1	1,2-Dimethylbenzene (below 16%) 1,4-Dimethylbenzene (below 15%)	1,3-Dimethylbenzene (below 69%)	(415)
1	1,2-Dimethylbenzene (12.5%) 1,4-Dimethylbenzene (12.1%)	1,3-Dimethylbenzene (53.9%)	(415)
1	1,4-Dimethylbenzene (below 4%)	1,3-Dimethylbenzene (below 96%)	(415)
1	1,2-Dimethylbenzene (below 11.7%) 1,4-Dimethylbenzene (below 17.1%)	1,3-Dimethylbenzene (below 61.2%)	(415)
1	1,2-Dimethylbenzene (11.1%) 1,4-Dimethylbenzene (11.8%)	1,3-Dimethylbenzene (46.6%)	(415)
1	1,2-Dimethylbenzene (below 13.4%) 1,4-Dimethylbenzene (below 14.4%)	1,3-Dimethylbenzene (below 68.2%)	(415)
1	1,2-Dimethylbenzene (below 12.8%) 1,4-Dimethylbenzene (below 14.4%)	1,3-Dimethylbenzene (below 53.6%)	(415)
1	1,2-Dimethylbenzene (10.2%) 1,4-Dimethylbenzene (12.2%)	1,3-Dimethylbenzene (41.7%)	(415)
1	1,2-Dimethylbenzene (below 18%) 1,4-Dimethylbenzene (below 10%)	1,3-Dimethylbenzene (below 72%)	(415)
1	1,3-Dimethylbenzene (mainly), 1,4-Dimethylbenzene (78.6%)	Low-boiling hydrocarbon (2.86%) Mesitylene (mainly), Pseudocumene (5.7%)	(245)
1	1,3-Dimethylbenzene (mainly), 1,4-Dimethylbenzene (33.3%)	Benzene (1.67%) Toluene, crude (20.8%) Mesitylene (mainly), Pseudocumene (20.8%) Durene (5%) Tetramethylanthracene (m.p. 290°) (0.083%)	(6)
1	1,3-Dimethylbenzene (1.2%)	Gas (0.9%) Toluene (2.1%) 1,4-Dimethylbenzene (88.2%) Condensed products (6.9%)	(139)
1	1,3-Dimethylbenzene (3.7%)	Gas (3.7%) Toluene (4.6%) 1,4-Dimethylbenzene (73.1%) Condensed products (14.1%)	(139)
1	1,3-Dimethylbenzene (4.1%)	Gas (8.9%) Toluene (7.9%) 1,4-Dimethylbenzene (57.3%) Condensed products (17.8%)	(139)
1	1,3-Dimethylbenzene (3.8%)	Gas (14.8%) Toluene (13.3%) 1,4-Dimethylbenzene (45.4%) Condensed products (19.3%)	(139)
1	1,3-Dimethylbenzene, crude (3.3%)	Gas Benzene (3.3%) Toluene (22%) 1,4-Dimethylbenzene (23.3%) 2,6-Dimethylanthracene and other residues (22%)	(28)

Table 35. Isomerization of Benzenes

Reactants: Substituted Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1,4-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.5%)	5	40–50
1,4-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	5	50
1,4-Dimethylbenzene	$AlCl_3$ HCl (gas)	(56%)	10 min.	55
1,4-Dimethylbenzene	$AlCl_3$ HCl (gas)	(55.7%)	0.25	94
1,4-Dimethylbenzene	$AlCl_3$ HCl (gas)	(16.7%)	6	100
Ethylbenzene	Porcelain tube used		(long)	moderate red-heat
Ethylbenzene	Porcelain tube used			moderate red-heat
1,2,4-Trimethylbenzene (Pseudocumene)	$AlCl_3$			
1,2,4-Trimethylbenzene	$AlCl_3$	(7.4%)	6	150–160
1,2,4-Trimethylbenzene	$AlCl_3$	(21.2%)	2	b.p.
1,3,5-Trimethylbenzene (Mesitylene)	$AlCl_3$ HCl (gas)	(9.1%)	4	150–160
1,2,3,5-Tetramethylbenzene (Isodurene)	H_2SO_4 (sulfonation) Later, hydrolysis of prehnitene sulfonic acid dihydrate at 140–150° by dilute H_2SO_4 and superheated steam	(78.6%)	10 days	at room (sulfonation)

with Saturated Side-Chains—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers	Other Products	References
1	1,3-Dimethylbenzene		(392)
1	1,2-Dimethylbenzene (below 11.6%) 1,3-Dimethylbenzene (below 63.1%)	1,4-Dimethylbenzene (below 8.3%)	(415)
1	1,2-Dimethylbenzene (0.6%) 1,3-Dimethylbenzene (64.3%)	1,4-Dimethylbenzene (35.1%)	(414)
1	1,2-Dimethylbenzene (below 14.4%) 1,3-Dimethylbenzene (below 27.9%)	1,4-Dimethylbenzene (below 47.7%)	(415)
1	1,3-Dimethylbenzene (50%)	Benzene (2%?) Mesitylene, Pseudocumene (5%?)	(245)
	1,4-Dimethylbenzene	Benzene Toluene Ethylbenzene Styrene Naphthalene Dihydronaphthalene (large %)	(63)
	1,4-Dimethylbenzene	Benzene Toluene Ethylbenzene (?) Styrene Phenylethyne Naphthalene Dihydronaphthalene (large %)	(61)
	1,3,5-Trimethylbenzene	Benzene Toluene 1,4-Dimethylbenzene Durene Isodurene	(7)
1	1,3,5-Trimethylbenzene (3.2–4%)	HCl CH_3Cl Benzene (2%) Toluene (8%) *m*-Xylene (mainly), *p*-Xylene (26–28%) Durene (8%) Isodurene (3.2%)	(290)
1	1,3,5-Trimethylbenzene (30.8%)	Toluene (15.4%) *m*-Xylene (mainly), *p*-Xylene (15.4%) Isodurene (mainly), Durene (11.5%) Anthracenes (small %)	(6)
1	1,2,4-Trimethylbenzene (small %)	CH_3Cl Benzene (small %) Toluene (small %) *m*-Xylene (large %) Durene (5%) Isodurene (16%)	(290)
1	1,2,3,4-Tetramethylbenzene (yield of sulfonic acid dihydrate was 50% of theory)	SO_2 (during sulfonation)	(558)

Table 35. Isomerization of Benzenes

Reactants: Substituted Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1,2,4,5-Tetramethylbenzene (Durene)	H_2SO_4 (sulfonation) Later, hydrolysis of prehnitene sulfonic acid dihydrate at 140–150° by dilute H_2SO_4 and superheated steam	(78.6%)	25 days	at room (sulfonation)
sec-Butylbenzene	$AlCl_3$	(20%)	4	140–145
"1,3-Dimethyl-4-*n*-propylbenzene"	$AlCl_3$	(20%)	4	100
"1,3-Dimethyl-4-isopropylbenzene"	$AlCl_3$	(17.9%)	3	55–60
1,2,4-Trimethyl-5-ethylbenzene	H_2SO_4+10% SO_3 Later, "50% H_2SO_4"+steam (hydrolysis)	(85%)	1 (sulfonation)	60–70 (sulfonation) 140–150 (hydrolysis)
1,3,5-Trimethyl-2-ethylbenzene	H_2SO_4+10% SO_3 Later, "50% H_2SO_4"+steam (hydrolysis)	(85%)	6 (sulfonation)	60–70 (sulfonation) 140–150 (hydrolysis)
"1,3-Dimethyl-4-*n*-butylbenzene"	$AlCl_3$	(17.8%)	4	100
"1,3-Dimethyl-4-*n*-butylbenzene"	$FeCl_3$ (anhydrous)	(20.1%)	2.25	80–100
"1,3-Dimethyl-4-isobutylbenzene"	$FeCl_3$ (anhydrous)	(20.4%)	2.25	80–100
"1,3-Dimethyl-4-*sec*-butylbenzene"	$AlCl_3$	(17.8%)	2.5	100
"1,3-Dimethyl-4-*sec*-butylbenzene"	$FeCl_3$ (anhydrous)	(20.1%)	1.5	80
"1,3-Dimethyl-4-*tert*-butylbenzene"	$AlCl_3$	(17.24%)	3.25	100

...with Branched Side-Chains—*Continued*

Products (% by weight on original ...)	Other Products	Ref.
SO₃ (sulfonation): 1,2,3,4-Tetramethylbenzene (yield of sulfonic acid dihydrate was 70% of theory) (90%)		(558)
Pentamethylbenzene (?) (15.6%)	Products, b.p. 120–190 (not investigated)	(571)
1,3-Dimethyl-5-isopropylbenzene (crude, 23.9%)		
1,3-Dimethyl-5-isopropylbenzene (90.6%)		
SO₃ (sulfonation): 1,2,4-Trimethyl-5-ethylbenzene (27.0%); Pseudocumene	1-Ethyl-2,4-dimethylbenzene (9.0%); Prehnitene (7.0%); Hydrocarbon, m.p. 173–175° (1%); Polymers (20%)	(559)
SO₃ (sulfonation): 1,2,4-Trimethyl-3-ethylbenzene (34.5%); Pseudocumene	1,3-Dimethyl-2-ethylbenzene (9.5%); Prehnitene (10.0%); Hydrocarbon, m.p. 185–186° (1%); Polymers (20%)	(559)
1,3-Dimethyl-5-t-butylbenzene (9.5%); m-Xylene	Fraction, b.p. 50–105° at 16 mm. Hg (14.5%); Fraction, b.p. 105–145° at 16 mm. Hg (27.0%)	(405)
1,3-Dimethyl-5-t-butylbenzene (41%); Fraction, b.p. 85–91° at 17 mm. Hg (3.7%)	Fraction, b.p. 94–105° at 17 mm. Hg (20%); Fraction, b.p. above 105° at 17 mm. Hg (18.5%)	(405)
1,3-Dimethyl-5-t-butylbenzene (52%); Fraction, b.p. 85–91° at 22 mm. Hg (4.2%)	Fraction, b.p. 94–105° at 22 mm. Hg (9.5%); Fraction, b.p. above 105° at 22 mm. Hg (28.6%)	(405)
1,3-Dimethyl-5-t-butylbenzene (40.9%); m-Xylene (9.5%)	Fraction, b.p. ... mm. Hg (2.7%); Fraction, b.p. 91–145° at ...	(405)

Table 35. Isomerization of Benzenes

Reactants: Substitute Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
"1,3-Dimethyl-4-*tert*-butylbenzene"	$AlCl_3$	(14.3%)	2	100
"1,3-Dimethyl-4-*tert*-butylbenzene"	$FeCl_3$ (anhydrous)	(20.2%)	1.5	80
1,3-Dipropylbenzene	$AlCl_3$	(25.3%)	22	100
1,4-Dipropylbenzene	$AlCl_3$		2	100
1,4-Dipropylbenzene	$AlCl_3$	(25.3%)	22	100
1,2,3,5-Tetraethylbenzene	H_2SO_4 (sulfonation) Later, hydrolysis of the resultant sulfonic acid monohydrate at 140° by dilute H_2SO_4 (50% by volume) and steam		15 min. at	100 (sulfonation)
1,2,4,5-Tetraethylbenzene	H_2SO_4 (sulfonation) Later, hydrolysis of the resultant sulfonic acid monohydrate at 140° by dilute H_2SO_4 (50% by volume) and steam		15 min. at	100 (sulfonation)
1,2,3,5-Tetraethylbenzene 1,2,4,5-Tetraethylbenzene (various mixtures)	H_2SO_4 (sulfonation) Later, hydrolysis of the resultant 1,2,3,4-tetraethylbenzene sulfonic acid monohydrate (84 grams) at 130–150° by "50 per cent H_2SO_4" (300 cc.) and steam	(80%)	15 min. at	100 (sulfonation)
1,2,4-Tripropylbenzene	$AlCl_3$		4	100
Hexaphenylethane	HCl (gas) Benzene (solvent)			
Hexaphenylethane	HCl (aqueous) Benzene (solvent)			
Hexaphenylethane ("Triphenylmethyl")	*m*-Xylene (solvent)			heated
Hexaphenylethane ("Triphenylmethyl")	Na Ether (solvent)			room
dl-2,3-Diphenylbutane			8	235–250
dl-3,4-Diphenylhexane	I_2			250–265
meso-3,4-Diphenylhexane	I_2			250–265

with Saturated Side-Chains (Continued)

Products	Yield (% by weight on original aromatic)	Other Products	References (Notes)
Fraction, b.p. 40–100° at 18–30 mm. Hg	(36%)	1,3-Dimethyl-5-ethylbenzene (45%)	(561)
Fraction, b.p. 105–115° at 30 mm. Hg	(5.5%)		
Fraction, b.p. 85–91° at 17 mm. Hg	(40%)	1,3-Dimethyl-5-propylbenzene (65%)	(561)
Fraction, b.p. 93–97° at 17 mm. Hg	(13.3%)		
Fraction, b.p. above 97° at 17 mm. Hg	(10%)		
Propylbenzene	(7%)	1,3-Dipropylbenzene (60.8%)	(37)
1,3,5-Tripropylbenzene			
Propylbenzene	(1.5%)	1,3-Dipropylbenzene (15.73%)	(37)
Dipropylbenzene	(8.44%)		
Alkylated benzene	(14%)		
1,2,3,4-Tetraethylbenzene (over 85%)			(558a)
1,2,3,4-Tetraethylbenzene (over 85%)			(558a)
1,2,3,4-Tetraethylbenzene (81–83%)			(558a)
Tripropylbenzene (30%) (mainly)		1,3-Dipropylbenzene (28%)	(37)
1,4-Dipropylbenzene (12%)			
Tetrapropylbenzene			
p-Benzohydryl-tetraphenylmethane			(222)
p-Benzohydryl-tetraphenylmethane			(222)
p-Benzohydryl-tetraphenylmethane			(516)
p-Benzohydryl-tetraphenylmethane			(519) (N_2)
meso-2,3-Diphenylbutane			(334)
meso-3,4-Diphenylhexane			(334)
dl-3,4-Diphenylhexane			(334)

Table 36. Isomerization

Reactants: Alkenyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C)
1-Phenylpropene-1 (Propenylbenzene)	Dry caustic-alkali			heated
3-Phenylpropene-1 (Allylbenzene)	Charcoal		2–3 drops feed per 23.56 cc. cat. per min.	300
Allylbenzene	Ni on asbestos			360
Allylbenzene	Pd			300
Allylbenzene	Al_2O_3			200–225
Allylbenzene	Cr_2O_3		2–3 drops feed per 23.56 cc. cat. per min.	220
Allylbenzene	Fe_2O_3		2–3 drops feed per 23.56 cc. cat. per min.	220
Allylbenzene	SiO_2 gel		2–3 drops feed per 23.56 cc. cat. per min.	300
Allylbenzene	Clay		2–3 drops feed per 23.56 cc. cat. per min.	300
Allylbenzene	Infusorial earth			500
Allylbenzene	Infusorial-earth briquettes		(2 or 3 passes)	500
Allylbenzene	Dry caustic alkali			heated
Allylbenzene	KOH C_2H_5OH			b.p.
Allylbenzene	KOH C_2H_5OH Propylbenzene (diluent)			130
4-Phenylbutene-1	"Pyrex" glass tube		28 sec.	550
4-Phenylbutene-1	Pt, 30% Charcoal, 70%			300
4-Phenylbutene-1	Al_2O_3		0.1 ml. feed per minute (1 pass)	225 or 250 or 300
4-Phenylbutene-1	Cr_2O_3		0.1–0.15 ml. feed per minute	225 or 250
1-Phenylbutene-2	Alcoholic potash			b.p.
1-Phenylbutene-2	Alcoholic potash		(long)	160–180
5-Phenylpentene-1	Cr_2O_3		0.1–0.15 ml. feed per minute	250
1-Phenyl-3-methylbutene-2	H_2SO_4			
1-Phenyl-3-methylbutene-2	H_3PO_4, 85% H_2O, 15%			b.p.
1-Phenyl-3-methylbutene-2	Alcoholic potash			180
5-Phenylpentene-1	H_2SO_4			
5-Phenylpentene-1	H_2SO_4, 90% H_2O, 10%	(74.3%)	40–50 min. at then 2 at	9–10 25–30

of Alkenyl Benzenes

Products (% by weight on original unit)	Pressure (atm.)	Other Products	Ref.
Allylbenzene (74%)			(2)
Propenylbenzene (38–49%)			(339)
Propenylbenzene (73%)			(338)
Propenylbenzene (100%)			(348)
Propenylbenzene			(338)
Propenylbenzene (93%)			(339)
Propenylbenzene (72%)			(339)
Propenylbenzene (53%)			(339)
Propenylbenzene (35%)			(339)
Propenylbenzene			(457)
Propenylbenzene			(456)
Propenylbenzene			(2)
Propenylbenzene			(584)
Propenylbenzene			(309)
1-Phenylbutene-1 (0.07%)			(2)
1-Phenylbutene-2; Gaseous olefines (mainly ethane) (1.53%)			(2)
(0.61%)			
Propene (4.13%)			
Benzene and toluene (19.5%)			
Butene (below 19.8%)			
2-Phenylbutene-1 (27%)			
Naphthalene (about 10%)			
1-Phenylbutene-1; 1-Phenylbutene-2			(346)
1-Phenylbutene-1 (80–93%) (CO_2)			(346a)
1-Phenylbutene-1 (CO_2)			(346a)
1-Phenylbutene-1			(183)

Table 36. Isomerization of

Reactants			
Alkenyl Benzene	Catalyst (Per cent by weight on aromatic+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Phenylpentene-2	H_2SO_4		
1-Phenylpentene-2	KOH (25%) C_2H_5OH (50%)	1 day	150
6-Phenylhexene-1			
6-Phenylhexene-1	H_2SO_4, 90% } H_2O, 10% } (74.2%)	40–50 min. then 2	at 9–10 at 25–30
o-Allyltoluene	Al_2O_3		220–225
m-Allyltoluene	Al_2O_3		220–225
p-Allyltoluene	Al_2O_3		220–225
p-Allyltoluene	Pt, 30% } Charcoal, 70% }		300
p-Diallylbenzene	Al_2O_3 (dehydrated at 360–400° C.)	2–3 drops feed per 31.4 cc. cat. per min.	300
1,1-Diphenylethylene	Infusorial-earth briquettes	(2 or 3 passes)	500
cis-1,2-Diphenylethylene (Isostilbene)	Sunlight		
Isostilbene	Sunlight		
Isostilbene	Sunlight	(long)	
Isostilbene		1	170–180
Isostilbene		1	170–178
Isostilbene			heated
Isostilbene			above 200
Isostilbene		distillation time	277–307
Isostilbene	"Pyrex" reaction vessel	91.7 min.	320
Isostilbene	"Pyrex" reaction vessel	200.3 min.	320
Isostilbene	"Pyrex" reaction vessel	23.4 min.	341
Isostilbene	"Pyrex" reaction vessel	62.7	341
Isostilbene	Ultraviolet light (90% being 2537 Å.) C_2H_5OH, 1.0 volume } Ether, 2.5 volumes } (solvent) Isopentane, 2.5 volumes } Air absent	1	liquid-air temperature
Isostilbene (0.010 molar solution)	Ultraviolet light (90% being 2537 Å.) C_2H_5OH, 1 volume } Ether, 9 volumes } (solvent)	1 or 3	−90
Isostilbene (0.00002 molar solution)	Ultraviolet light (2537 Å.) "Iso-octane" (solvent)	0–4000 sec.	20
Isostilbene (0.005 molar solution)	Ultraviolet light (2537 Å.) "Iso-octane" (solvent)	0–1	20
Isostilbene	Li Ether (solvent) Later, Hg and CO_2	Li: 24 at Hg: "overnight" at	room room
Isostilbene	Stilbene-dilithium	"instantly"	heat evolved
Isostilbene	Na Ether (solvent) Later, C_2H_5OH	Na: 2 days at	room
Isostilbene	Na Ether (solvent) Later, Hg	Na: 14 days at	room
Isostilbene	Stilbene-disodium	"instantly"	heat evolved

Alkenyl Benzenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers		Other Products		Reference
1	1-Methyltetralin				(73)
bomb	1-Phenylpentene-1				(309)
1	1-Ethyltetralin				(73)
1	1-Ethyltetralin	(65%)			(471)
	o-Propenyltoluene				(338)
	m-Propenyltoluene				(338)
	p-Propenyltoluene				(338)
(CO_2)	*p*-Propenyltoluene	(84%)	*p*-Allyltoluene	(16%)	(345)
(CO_2)	*p*-Allylpropenylbenzene, 1 part; *p*-Dipropenylbenzene, 5 parts				(342a)
1	Stilbene				(456)
1	Stilbene				(428a)
1	Stilbene				(652)
1	Stilbene				(572)
	Stilbene				(567)
	Stilbene	(large %)			(572)
1	Stilbene				(570)
	Stilbene				(652)
1	Stilbene				(652)
sub-atm.	Stilbene	(82.8%)	Isostilbene	(17.2%)	(306)
sub-atm.	Stilbene	(83.0%)	Isostilbene	(17.0%)	(306)
sub-atm.	Stilbene	(81.7%)	Isostilbene	(19.3%)	(306)
sub-atm.	Stilbene	(82.2%)	Isostilbene	(17.8%)	(306)
1	Stilbene		Isostilbene		(350a)
1	Stilbene		Isostilbene		(350a)
1	Stilbene		Isostilbene Yellow substance		(350a)
1	Stilbene (29% of the excited molecules)		Isostilbene (unexcited molecules +68% of the excited molecules) Yellow substance (3% of the excited molecules)		(350a)
1	Stilbene				(516)
1					
1	Stilbene				(680)
1	Stilbene				(516)
1	Stilbene				(516)
1	Stilbene				(680)

Table 36. Isomerization of

Reactants: Alkenyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)	Contact Time (hours)	Temp. (°C.)
Isostilbene	O_2	403 min.	214
Isostilbene	O_2	23.3	214
Isostilbene	Br_2 (trace) Sunlight		
Isostilbene	Br_2 and sunlight CS_2 (solvent)		
Isostilbene	Br_2 and HBr in the dark C_6H_6 (?)		room
Isostilbene	I_2 (trace) Sunlight	(short)	
Isostilbene	I_2 (trace) Sunlight	(short)	
Isostilbene	BF_3 and ether complex (b.p. 125°) in the dark	12	room
Isostilbene	BF_3 and ether complex (b.p. 125°) in the dark	24	room
Isostilbene	BF_3 and ether complex (b.p. 125°) in the dark	30	room
Isostilbene	BF_3 and ether complex (b.p. 125°) in the dark	36	room
Isostilbene	BF_3 and ether complex (b.p. 125°) in the dark	72	room
Isostilbene	BF_3 in the dark CCl_4 (solvent)	16	room
Isostilbene	BF_3 in the dark CCl_4 (solvent)	18	room
Isostilbene	BF_3 in the dark CCl_4 (solvent)	19	room
Isostilbene	HBr and O_2 in the dark	few min.	room
Isostilbene (5% solution)	HBr and air in the dark C_6H_6 (solvent)	20–30 min.	room
Isostilbene	HBr and air in the dark C_6H_6 (solvent)	2	room
Isostilbene	HBr and air Diphenylamine	1	room
Isostilbene	HBr and air Catechol	20	room
Isostilbene	HBr and air in the light Ethyl mercaptan C_6H_6 (?)		room
Isostilbene	HBr and air in the light Hydroquinone C_6H_6 (?)		room
Isostilbene	HBr Reduced Cu	over 20	room
Isostilbene	HBr Reduced Fe	0.5–4	room
Isostilbene	HBr in the dark Reduced Ni	0.5–3	room
Isostilbene	HBr in the dark Reduced Ni	below 0.5	100
Isostilbene (5–10% solution)	HBr (0.015–0.08N) in the dark Reduced Ni (0.1–0.5 g. per 4 cc. solution) C_6H_6 (solvent)	1–4 days	room
Isostilbene	HBr (large %) Reduced Ni C_6H_6 (?)		room

Alkenyl Benzenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers		Other Products	References
1 (O_2)	Stilbene	(4.3%)	An acid	(578)
1 (O_2)	Stilbene	(12.8%)	An acid	(578)
1	Stilbene			(652)
1	Stilbene			(567)
1	No Stilbene			(303)
1	Stilbene			(652)
1	Stilbene			(572)
1	Stilbene	(below 10%)		(447)
1	Stilbene	(38.1%)		(447)
1	Stilbene	(74.8%)		(447)
1	Stilbene	(92.3%)		(447)
1	Stilbene	(92.2%)		(447)
1	Stilbene	(81.0%)		(447)
1	Stilbene	(93.1%)		(447)
1	Stilbene	(93.1%)		(447)
1	Stilbene			(607)
1	Stilbene	(over 50%)		(608)
1	No stilbene			(303)
1	Stilbene	(20%)		(608)
1	No stilbene			(608)
1	No stilbene			(303)
1	No stilbene			(303)
1	Stilbene			(608)
1	Stilbene			(608)
1	Stilbene			(607)
1	Stilbene			(607)
1	No stilbene			(608)
1	Stilbene	(small %)		(608)

Table 36. Isomerization of

Reactants: Alkenyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)	Contact Time (hours)	Temp. (°C.)
Isostilbene	HBr Pd black	over 20	room
Isostilbene	HBr Pt black	over 20	room
Isostilbene	HBr Ascaridole C_6H_6 (solvent)	few min.–30 min.	room
Isostilbene	HBr in the dark Benzoyl peroxide	few min.	room
Isostilbene	HBr Benzoyl peroxide C_6H_6 (solvent)	few min.-30 min.	room
Isostilbene	HBr in sunlight C_6H_6 (solvent)	5–20 min.	room
Isostilbene	HBr in artificial light C_6H_6 (solvent)	5–20 min.	room
Isostilbene	HBr in sunlight Air absent	0.5–1.0 min.	room
Isostilbene	HBr in the dark		room
Isostilbene (5–10% solution)	HBr in the dark C_6H_6 (solvent)	1–4 days	room
Isostilbene	HBr in the dark C_6H_6 (solvent) Air absent	2	room
Isostilbene	HBr in the dark Air absent	0.5	100
Isostilbene	HBr in the dark Catechol (0.005 g. per 0.2 cc. isostilbene) Air absent	0.5	100
Isostilbene	HBr in the dark Catechol	2	room
Isostilbene	HBr in sunlight Catechol		room
Isostilbene	HBr in the dark Reduced Ni (0.020 g. per 0.2 cc. isostilbene) Catechol (0.005 g. per 0.2 cc. isostilbene)	40	room
Isostilbene	HBr in the light Hydroquinone C_6H_6 (?) Air absent		room
Isostilbene	HBr in the dark Hydroquinone C_6H_6 (solvent)	2	room
Isostilbene	HBr in the dark Thiophenol C_6H_6 (solvent)	2	room
Isostilbene	HBr in the light Ethyl mercaptan C_6H_6 (?) Air absent		room
Isostilbene	HBr in sunlight Diphenylamine	1 min.	room
Isostilbene	HBr in the dark Diphenylamine		room
Isostilbene	Diphenylamine in the dark		room
Isostilbene	HBr in the dark Reduced Ni Diphenylamine		room

Alkenyl Benzenes—*Continued*

Products, % by weight on original	Pressure (atm)	Refs.	Other Products
Stilbene	1	(608)	
Stilbene	1	(608)	
(100%) Stilbene	1	(303)	
Stilbene	1	(607)	
(100%) Stilbene	1	(303)	
Stilbene	1	(303)	
Stilbene	1	(303)	
Stilbene	sealed tube	(608)	
No stilbene	1	(607)	
No stilbene	1	(608)	
No stilbene	1	(303)	
Stilbene	sealed tube	(608)	
No stilbene	sealed tube	(608)	
No stilbene	1	(303)	
No stilbene	1	(608)	
No stilbene	1	(608)	
No stilbene	1	(303)	
No stilbene	1	(303)	
No stilbene	1	(303)	
[illegible]	1	(303)	

Table 36. Isomerization of

Reactants: Alkenyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)	Contact Time (hours)	Temp. (°C.)
Isostilbene	HCl	4	190
Isostilbene	HCl, 20% } H_2O, 80% }		b.p.
Isostilbene	HCl Ascaridole C_6H_6 (solvent) (In the light or dark)		room
Isostilbene	HCl Benzoyl peroxide C_6H_6 (solvent) (In the light or dark)		room
Isostilbene	HCl Catechol C_6H_6 (solvent) (In the light or dark)		room
Isostilbene	HCl Hydroquinone C_6H_6 (solvent) (In the light or dark)		room
Isostilbene	HCl Thiophenol C_6H_6 (solvent) (In the light or dark)		room
Isostilbene	HNO_3 (fuming)	several min.	
Isostilbene	HNO_3 (fuming)	0.5	room
Isostilbene	HNO_3 (fuming)		
Isostilbene	$C_6H_5 . CO_2H$	400 min.	214
Isostilbene	$C_6H_5 . CO_2H$	3400 min.	214
Isostilbene	$C_6H_5 . CO_2H$	400 min.	223
Isostilbene	$C_6H_5 . CO_2H$	20	223
Isostilbene	$C_6H_5 . CO_2H$		200
trans-1,2-Diphenylethylene (Stilbene)	"Pyrex" reaction vessel	16.6 min.	320
Stilbene	"Pyrex" reaction vessel	33.0 min.	320
Stilbene	"Pyrex" reaction vessel	61.0 min.	320
Stilbene	"Pyrex" reaction vessel	10.8 min.	341
Stilbene	"Pyrex" reaction vessel	27.3 min.	341
Stilbene	Ultraviolet light (3130 Å.) C_6H_{14} (solvent)	10–60 min.	room
Stilbene	Ultraviolet light (2537 Å.) "Iso-octane" (solvent)		20
Stilbene	Ultraviolet light C_6H_6 (solvent)		room
Stilbene	Ultraviolet light C_6H_6 (solvent)	8 days	
Stilbene	$C_6H_5 . CO_2H$		200
o-Phenyl-1,1-diphenylethylene	PCl_5		
1,1,3-Triphenylpropene-1	H_2SO_4 (94.8%)	8 days	room

Alkenyl Benzenes—*Continued*

Pressure (atms.)	Products— (Per cent by weight on original aromatic) Isomers		Other Products		References
1 (N_2)	Stilbene				(578)
1	Stilbene				(570)
1	No stilbene				(303)
1	No stilbene				(303)
1	No stilbene				(303)
1	No Stilbene				(303)
1	No stilbene				(303)
	Stilbene				(567)
1	Stilbene	(large %)			(572)
	Stilbene				(300)
1 (N_2)	Stilbene	(2.8%)			(578)
1 (N_2)	Stilbene	(16.8%)	Decomposition products		(578)
1 (N_2)	Stilbene	(5.65%)			(578)
1 (N_2)	Stilbene	(13.7%)			(578)
1 (N_2)	Stilbene	(96%)	Isostilbene	(4%)	(578)
sub-atm.	Isostilbene	(4.3%)	Stilbene	(95.7%)	(306)
sub-atm.	Isostilbene	(6.0%)	Stilbene	(94.0%)	(306)
sub-atm.	Isostilbene	(6.0%)	Stilbene	(94.0%)	(306)
sub-atm.	Isostilbene	(6.3%)	Stilbene	(93.7%)	(306)
sub-atm.	Isostilbene	(7.6%)	Stilbene	(92.4%)	(306)
1	Isostilbene		Stilbene		(556)
1	Isostilbene (35% of the excited molecules)		Stilbene (unexcited molecules+the 17% of excited molecules that do not fluoresce+the 48% of excited molecules that do fluoresce)		(350a)
1	Isostilbene		Stilbene		(350a)
1	Isostilbene	(9.0%)			(567)
1 (N_2)	Isostilbene	(4.0%)	Stilbene	(96.0%)	(578)
	9-Phenyl-9,10-dihydrophenanthrene				(50)
1	1,3-Diphenylindane	(16%)	1,1,3-Triphenylpropene-1		(517)

Table 36. Isomerization of

Reactants: Alkenyl Benzene	Catalyst (Per cent by weight on aromatic + catalyst)		Contact Time (hours)	Temp. (°C.)
1,1,3-Triphenylpropene-1	Li Ether (solvent) Later, diphenylbromomethane (9.2 grams per 10 grams of 1,1,3-triphenylpropene-1)			room
1,2,3-Triphenylpropene	Unstated (work of Ramart and Amagat referred to)		unstated	unstated
1,1,3,3-Tetraphenylpropene	Li Ether (solvent) Later, C_2H_5OH	(3%) (92%)	8 days to dissolve Li	room
1,2,3,3-Tetraphenylpropene-1	Na and (? ether) Later, Hg		reacts slowly with Na	room
1,1,3,3,3-Pentaphenylpropene	H_2SO_4 $CH_3 . CO_2H$	(3.8%) (91.7%)	3	b.p.
1,3-Diphenylbutene-1	H_2SO_4	(trace)	3–4 years	room
1,3-Diphenylbutene-1	H_2SO_4, 50% H_2O, 50%	(93.5%)	40	b.p.
2,3-Diphenylbutene-2 (m.p. 104°, β-form)	H_2SO_4-treated pumice		"several minutes"	heated
1,1,3,3-Tetraphenylbutene	I_2	(9.09%)	over 6	100
1,1,3,3-Tetraphenylbutene	Li Ether (solvent) Later, C_2H_5OH		6 days to dissolve Li	room
1,1,3,3-Tetraphenylbutene	"Floridin"		6 days	215
1,1,3,3-Tetraphenylbutene	$SnCl_4$ C_6H_6 (solvent)	(4.7%) (83.4%)	1 week	room
1,1,3,3-Tetraphenylbutene	$SnCl_4$ HCl (gas) C_6H_6 (solvent)	(4.7%) (83.4%)	1 week	room
1,1,3,3-Tetraphenylbutene	$SnCl_4$ (50 cc. per 5 g. of the butene)		1 week	b.p.
1,1,3,3-Tetraphenylbutene	H_2SO_4		(long)	room
1,1,3,3-Tetraphenylbutene	Dimethyl sulfate	(26.5%)	6	100
1,2,3,4-Tetraphenylbutene-1 (m.p. 96°)	Na Ether (solvent) Later, C_2H_5OH			room
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Na Ether (solvent) Later, C_2H_5OH (?)		Na: 3 days	room
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Na Amyl alcohol	(5.5%) (86%)		b.p.
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Benzene (solvent) HCl (to saturation) $SnCl_4$ After 7 days, ice-cold fuming hydrochloric acid	(82.5%) (14.3%)	7 days	room
1,2,3,4-Tetraphenylbutene-1 (m.p. 150°)	Red phosphorus HI soln. (d. = 1.7) $CH_3 . CO_2H$	(4.0%) (15.2%) (78.5%)	4	b.p.
1,2,3,4-Tetraphenylbutene-2 (m.p. 80°)				distillation temp.

Alkenyl Benzenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers		Other Products		References
1	1,3-Diphenylindane	(10%)	1,1,2,2-Tetraphenylethane	(large %)	(518)
	1,2-Diphenylindane				(52)
1	1,2,3-Triphenylindane				(516)
1	1,1,2,3-Tetraphenylpropene-1		1,1,2,3,4,5,6,6-Octaphenylhexadiene-1,5		(53)
1	1,1,3,3-Tetraphenylindane				(316)
1	1-Methyl-3-phenylindane (?)	(100%)	1,3-Diphenylbutene-1	(trace)	(569)
1	1-Methyl-3-phenylindane	(63.3%)	Polymers	(20%)	(468)
1	2,3-Diphenylbutene-2 (m.p. 65°, α-form)	(over 5%)	2,3-Diphenylbutene-2 (m.p. 104°, β-form)	(over 27.5%)	(458)
1	1-Methyl-1,3,3-triphenylindane (?)				(54)
1	1,1,4,4-Tetraphenylbutene-2 1-Methyl-1,2,3-triphenylindane	(43%)	1,1-Diphenylethane 1,1-Diphenylethylene 1,1,4,4-Tetraphenylbutadiene-1,3		(55)
bomb	1-Methyl-1,3,3-triphenylindane				(332)
1	No isomers		1,1,3,3-Tetraphenylbutene 1,1-Diphenylethylene	(80%) (14%)	(522)
1	1-Methyl-1,3,3-triphenylindane	(90%)			(522)
1	1-Methyl-1,3,3-triphenylindane	(90%)			(522)
1	1-Methyl-1,3,3-triphenylindane				(54)
1	1-Methyl-1,3,3-triphenylindane	(88.9%)			(43a)
1	1,2,3,4-Tetraphenylbutene-2 (m.p. 80°)				(57)
1	1-Benzyl-2,3-diphenylindane 1,2,3,4-Tetraphenylbutene-2 (m.p. 80°)	(small %)			(57)
1	1-Benzyl-2,3-diphenylindane	(30%)	1,2,3,4-Tetraphenylbutane		(57)
1	1-Benzyl-2,3-diphenylindane				(57)
1	1-Benzyl-2,3-diphenylindane				(57)
high vacuum	1-Benzyl-2,3-diphenylindane				(57)

Table 36. Isomerization of

Reactants: Alkenyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1,2,3,4-Tetraphenylbutene-2 (m.p. 80°)	Na Ether (solvent) Later, C_2H_5OH		Na: 1 week	room
2,4-Diphenyl-4-methyl-pentene-2	$AlCl_3$ ("equimolar" with the diphenylmethyl-pentene) Benzene (solvent)		2 days	room
2,4-Diphenyl-4-methyl-pentene-2	$SnCl_4$	(9.09%)	20	room

Table 37. Isomerization

Reactants: Alkadienyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
Phenylpropadiene	Alcoholic potash		6.5	105–110
Tetraphenylpropadiene	I_2 Benzene (solvent)	(0.7%) (92.3%)	12	room
Tetraphenylpropadiene	I_2 Benzene (solvent)	(0.7%) (92.3%)		heated
Tetraphenylpropadiene	HBr (gas)		(long)	room
Tetraphenylpropadiene	HBr (gas) $CH_3 . CO_2H$			room
Tetraphenylpropadiene	HCl (gas)		(long)	room
Tetraphenylpropadiene	20% HCl (aqueous)	(90.9%)		b.p.
Tetraphenylpropadiene	HCl (gas) $CH_3 . CO_2H$ (solvent)		several	room
Tetraphenylpropadiene	HCl (gas) $CH_3 . CO_2H$ (solvent)		5 min.	b.p.
Tetraphenylpropadiene	$CH_3 . CO_2H$		8	b.p.
Triphenyl-(1-naphthyl)-propadiene	HCl (gas) $CH_3 . CO_2H$ (solvent)			b.p.
Triphenyl-(1-naphthyl)-propadiene	*p*-Toluenesulfonic acid Benzene (solvent)			b.p.
1,3-Diphenyl-1-*p*-tolyl-3-(1-naphthyl)propadiene	HCl (gas) $CH_3 . CO_2H$ (solvent)			b.p. (?)
d-1,3-Diphenyl-1,3-di-(1-naphthyl)propadiene	Decalin (solvent)	(95%)	48	190
d-1,3-Diphenyl-1,3-di-(1-naphthyl)propadiene	Decalin (solvent)		9.5	b.p.
dl-1,3-Diphenyl-1,3-di-(1-naphthyl)propadiene	I_2 Benzene (solvent)	(0.7%) (92.3%)	1	100
dl-1,3-Diphenyl-1,3-di-(1-naphthyl)propadiene	HCl (gas) $CH_3 . CO_2H$ (solvent)	(99.9%)	5 min.	b.p.
1,1,3-Triphenylbutadiene-1,2	H_2SO_4 $CH_3 . CO_2H$ (solvent)	(5%) (87%)	0.25	heated (?)
1,1,3-Triphenylbutadiene-1,2	$CH_3 . CO_2H$	(90%)	4	b.p.
1,1,3-Triphenylbutadiene-1,2	Acetic anhydride	(90%)	4	b.p.
1-Phenylbutadiene-1,3	"Floridin"		0.05 g. feed per minute	290–300

Alkenyl Benzenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers		Other Products		References
1	1-Benzyl-2,3-diphenylindane	(30%)	1,2,3,4-Tetraphenylbutane		(57)
1	1,1,3-Trimethyl-3-phenylindane	(20%)	Resins		(51)
1	1,1,3-Trimethyl-3-phenylindane	(40%)			(51)

of Alkadienyl Benzenes

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers		Other Products		References
	1-Phenylpropyne-1				(214)
1	1,1,3-Triphenylindene		I_2	(10%)	(613)
1	1,1,3-Triphenylindene		I_2	(10%)	(613)
1	1,1,3-Triphenylindene		Addition product		(613)
1	1,1,3-Triphenylindene				(613)
1	1,1,3-Triphenylindene		Addition product		(613)
1	1,1,3-Triphenylindene				(613)
1	1,1,3-Triphenylindene				(613)
1	1,1,3-Triphenylindene				(317)
1	1,1,3-Triphenylindene				(613)
1	1,3,3-Triphenyl-3-α-naphthindene				(106)
1	1,3,3-Triphenyl-3-α-naphthindene				(106)
	1,3-Diphenyl-3-*p*-tolyl-3-α-naphthindene				(106)
sealed tube	*dl*-1,3-Diphenyl-1,3-di-(1-naphthyl)propadiene	(40%)			(358)
1	*dl*-1,3-Diphenyl-1,3-di-(1-naphthyl)propadiene	(small %)			(358)
1	1,3-Diphenyl-3-(1-naphthyl)-3-α-napthindene		I_2		(358)
1	1,3-Diphenyl-3-(1-naphthyl)-3-α-naphthindene				(358)
1	1-Methyl-1,3-diphenylindene (?) 1,1-Diphenyl-3-methylindene (?)				(679)
1	1,1,3-Triphenylbutadiene-1,3 (?)				(679)
1	1,1,3-Triphenylbutadiene-1,3 (?)				(679)
1	4-Phenylbutyne-1 (?)		Polymers	(65–70%)	(555)

Table 37. Isomerization of

Reactants: Alkadienyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic + catalyst)		Contact Time (hours)	Temp. (°C.)
cis-1-Phenylbutadiene-1,3	$CaCl_2$ wetted with dilute hydrochloric acid		"Overnight" at then (time of distillation) at	room 76
cis-cis-1,4-Diphenylbutadiene-1,3	Sunlight		2 months	
cis-cis-1,4-Diphenylbutadiene-1,3	Sunlight $CH_3 . CO_2H$	(98.6%)	17 days	
cis-trans-1,4-Diphenylbutadiene-1,3	Sunlight		0.25	
1,1,2,3-Tetraphenylbutadiene-1,3	$CH_3 . CO_2H$ H_2SO_4("a drop")		5 min.	b.p.
1,2,3,4-Tetraphenylbutadiene-1,3	Na Ether (solvent) Later, Hg for demetalation		Na: 3 days Hg: 1 day	room
1,2,3,4-Tetraphenylbutadiene-1,3	$SnCl_4$ Benzene	(19%) (73%)		room

Table 38. Isomerization

Reactants: Alkapolyenyl Benzene	Reactants: Catalyst (Per cent by weight on aromatic + catalyst)		Contact Time (hours)	Temp. (°C.)
cis-1,4-Diphenylbutatriene	Sunlight			
cis-1,4-Diphenylbutatriene	Sunlight		14 days	
cis-1,4-Diphenylbutatriene	I_2 (trace) and sunlight		(long)	
1,1,5,5-Tetraphenyl-3-styrylpentadiene-1,4	Phenyl-lithium Ether (solvent) Later, CH_3OH in excess		2 days with C_6H_5Li	room
1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetraene-1,2,4,5	40%-Sodium amalgam Ether (solvent) Later, 10% solution of tetraphenylethylene dibromide		36	room
1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetraene-1,2,4,5	Sodium amalgam Ether (solvent) Later, solution of tetraphenylethylene dibromide			
1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetraene-1,2,4,5	HCl (gas) $CH_3 . CO_2H$	(93.6%)	48	b.p.
1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetraene-1,2,4,5	HCl $CH_3 . CO_2H$			heated (?)
1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetraene-1,2,4,5	H_2SO_4 $CH_3 . CO_2H$	(3.2%) (92.6%)	several	heated
yellow-1,8-Diphenyloctatetrene-1,3,5,7	Sunlight		3 months	
yellow-1,8-Diphenyloctatetrene-1,3,5,7	I_2 and sunlight $CHCl_3$ (solvent)		several days	

Alkadienyl Benzenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers	Other Products	References
1	*trans*-1-Phenylbutadiene-1,3 (100%)		(395)
11 mm. Hg			
1	*trans-trans*-1,4-Diphenylbutadiene-1,3		(572)
1	*trans-trans*-1,4-Diphenylbutadiene-1,3 (33.3%)		(572)
1	*trans-trans*-1,4-Diphenylbutadiene-1,3		(572)
1	1-Methyl-1,2,3-triphenylindene (100%)		(316a)
1	1-Benzylidene-2,3-diphenylindane (about 67% on the "product")	1-Benzyl-2,3-diphenylindane (about 33% on the "product") 1,2,3,4-Tetraphenylbutane	(57)
1	1-Benzyl-2,3-diphenylindene (60%)		(57)

of Alkapolyenyl Benzenes

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers	Other Products	References
1	*trans*-1,4-Diphenylbutatriene		(229)
1	*trans*-1,4-Diphenylbutatriene		(572)
1	*trans*-1,4-Diphenylbutatriene		(572)
1 (N_2)	1,1,5,5-Tetraphenyl-3-phenethylidene-pentadiene-1,4		(654)
1 (N_2)	Isomer "B," m.p. 179.3–180.3° (25.5%)		(3)
	Isomer "B," m.p. 179–180°		(175)
1	Isomer "A," m.p. 173–174° (60%)		(3)
1	Isomer "A," m.p. 176° (i.e., 1,1′-Di-*tert*-butyl-3,3′-diphenyl-1,1′-biindene)		(175)
1	Isomer "A"		(3)
1 (CO_2)	*white*-1,8-Diphenyloctatetrene-1,3,5,7		(566)
1 (CO_2)	*white*-1,8-Diphenyloctatetrene-1,3,5,7	Resin	(566)

Table 39. Isomerization

Reactants: Alkynyl Benzene	Reactants: Catalyst (Per cent by weight on alkynyl benzene+catalyst)		Contact Time (hours)	Temp. (°C.)
1-Phenylpropyne-1	$NaNH_2$		2	110
4-Phenylbutyne-1	Cr_2O_3		0.1 ml. feed per minute	250
4-Phenylbutyne-1	"Floridin"		0.05 g. feed per minute	250
1,1,4,4-Tetraphenylbutyne-2	NaOH C_2H_5OH			
1,1,4,4-Tetraphenylbutyne-2	C_2H_5ONa C_2H_5OH (solvent)	(9.5%) (88.9%)	1	100
1,1,4,4-Tetra-*p*-tolyl-butyne-2	C_2H_5ONa C_2H_5OH (solvent)	(9.0%) (89.5%)	3	b.p.
1,1-Diphenyl-4,4-dimethyl-pentyne-2 (or Na derivative)	H_2O			
1,3,3,4,4,6-Hexaphenylhexa-diyne-1,5	Petroleum ether (solvent)		1	room
Isomer (m.p. 179°) related to 1,3,3,4,4,6-Hexaphenyl-hexadiyne-1,5				m.p.
Isomer (m.p. 172–173°) related to 1,3,3,4,4,6-Hexa-phenylhexadiyne-1,5	HCl $CH_3 . CO_2H$ (solvent)		4	b.p.
Isomer (m.p. 179°) related to 1,3,3,4,4,6-Hexa-phenylhexadiyne-1,5	Xylene (solvent) and any one of the following substances: $K_3Fe(CN)_6$ HgO PbO Pb_3O_4 $K_2S_2O_8$			heated
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7				slowly melted
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Hexane (solvent) Air present	(96%)	3–250 min.	27.5
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Heptane (solvent)	(98%)	1	b.p.
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		12	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		2 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		5 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Ether (solvent)		few min.	50
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	Acetone (solvent)	(99%)	0.75	b.p.

of Alkynyl Benzenes

Products

Yield (% by weight on original alkyne)

Isomers | Other Products

3-Phenylpropyne (after hydrolysis of the Na derivative) (67%) (30) (81)

Yellow (Polymers) (25%) (44)

4-Phenylbutadiene-1,2 (?) (40%)

1,1,4,4-Tetraphenylbutadiene-1,3 (85)

1,1,4,4-Tetraphenylbutadiene-1,3 (84)

1,1,4,4-Tetra-p-tolylbutadiene-1,3 (86)

1,1-Diphenyl-4,4-dimethylpentadiene-1,2 (504)

Isomer (m.p. 160–165°; 169° when pure) (303)

Isomer (m.p. 249°) (647)

Isomer (m.p. 261–262°) (20%) (249)

Isomer (m.p. 225°) (10%) (648)

1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetrene-1,2,4,5 (504)

1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetrene-1,2,4,5 Oxidation products (504)

1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetrene-1,2,4,5 (68%) (504)

1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexa- (504)

Table 39. Isomerization of

Reactants: Alkynyl Benzene	Catalyst (Per cent by weight on alkynyl benzene+catalyst)	Contact Time (hours)	Temp. (°C.)
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	1% Sodium amalgam Ether (solvent) Later, C_2H_5OH	40	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	1% Sodium amalgam Ether (solvent) Later, C_2H_5OH	5 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetraphenyldecadiyne-3,7	1% Sodium amalgam Ether (solvent) Later, C_2H_5OH	8 days	room
2,2,9,9-Tetramethyl-5,5,6,6-tetra-biphenylyldecadiyne-3,7	Toluene (solvent)	10	room
3,10-Dimethyl-3,10-diethyl-6,6,7,7-tetraphenyldodeca-diyne-4,8		(short)	0
3,10-Dimethyl-3,10-diethyl-6,6,7,7-tetraphenyldodeca-diyne–4,8	Ether (solvent)	(long)	room

Table 40. Isomerization of Condensed Aromatics (Indanes, Indenes,

Reactants: Condensed Aromatic	Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1-(1,5-Dimethyl-4-hexenylidene)indene	H . CO_2H	(79.1%)	12	140
3-Phenylindene	Pumice			dark-red heat
3-*p*-Tolylindene	Pumice			dark-red heat
1-Benzylindene	KOH CH_3OH (solvent)			
1-Benzylindene	CH_3OK CH_3OH (solvent)		12	room
1-Diphenylmethylene-indane	Conc. hydrochloric acid		1	heated
1-Benzhydrylindene	KOH CH_3OH (solvent)			
1-Benzhydrylindene	CH_3OK CH_3OH (solvent)		24	room
1,2-Diphenylindene	KOH			
1,2-Diphenylindene	KOH C_2H_5OH (solvent)			b.p.
1,2-Diphenylindene	KOH C_2H_5OH (solvent)	(0.6%) (89%)		b.p.
1,3-Dibenzylidene-indane (?)			(long)	over 213
1,3-Dibenzylidene-indane (?)			time of distillation	250–260
1-Benzhydryl-3-*sec*-butyl-indene (?) of m.p. 121–123°	CH_3OK CH_3OH (solvent)		0.5–1.0	b.p.

Alkynyl Benzenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original alkynyl benzene) Isomers	Other Products	References
1 (N_2)	1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetrene-1,2,4,5 (?)+ (?) Isomer "B" of m.p. 181° (70% total)		(564)
1 (N_2)	1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetrene-1,2,4,5 (?)+ (?) Isomer "B" of m.p. 181°		(564)
1 (N_2)	1,1,6,6-Tetraphenyl-3,4-di-*tert*-butylhexatetrene-1,2,4,5 (?)+ (?) Isomer "B" of m.p. 181°		(564)
1	Isomer (m.p. 166°)		(592)
1	Isomer (m.p. 108°)		(242)
sub-atm.	Isomer (m.p. 106.5–108°) (50%)		(242)

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes)

Pressure (atms.)	Products (Per cent by weight on original condensed aromatic) Isomers	Other Products	References
	1-Isopropyl-4-methyl-2,3-dihydrofluorene (?)		(491)
16 mm. Hg (CO_2)	2-Phenylindene (33%)		(88)
16 mm. Hg (CO_2)	2-*p*-Tolylindene (16.5%)		(88)
	3-Benzylindene		(127)
1	3-Benzylindene		(126)
1	3-Benzhydrylindene		(126)
	3-Benzhydrylindene		(127)
1	3-Benzhydrylindene		(126)
	2,3-Diphenylindene		(230)
1	2,3-Diphenylindene		(428)
1	2,3-Diphenylindene		(69)
1	1-Benzylidene-3-benzylindene		(579)
12 mm. Hg	1-Benzylidene-3-benzylindene		(579)
1	1-*sec*-Butyl-3-benzhydrylindene (?) of m.p. 94–95°		(656)

Table 40. Isomerization of Condensed Aromatics (Indanes, Indenes,

Reactants: Condensed Aromatic	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1-Benzylidene-3-*p*-methylbenzylindene	KOH CH_3OH (solvent)			b.p.
1-*p*-Methylbenzylidene-3-benzylindene	KOH CH_3OH (solvent)			b.p.
1-*p*-Isopropylbenzylidene-3-benzylindene	CH_3OK CH_3OH (solvent)		10	b.p.
1-Benzylidene-3-benzhydrylindene	CH_3OK CH_3OH (solvent)		1	b.p.
1,1,3-Triphenylindene	Na			
1-Methyl-1,3,3-triphenylindane	"Floridin"		6 days	215
1-Biphenylene-3-phenylindene	40%-Sodium amalgam (an excess) Ether (solvent) Alcohol (for demetalation)		2 days for metalation	room
1-Biphenylene-3-phenylindene	Li (an excess) Ether (solvent)		3 days	
1,2-Diphenyl-3-*p*-tolylindene	40%-Sodium amalgam (an excess) Ether (solvent)		3	room
1,2-Diphenyl-3-*p*-tolylindene	Alcoholic potash (5% solution) (used 15 cc. per 0.5 g. aromatic)		1.25	b.p.
1-*p*-Tolyl-2,3-diphenylindene	40%-Sodium amalgam (an excess) Ether (solvent)		3	room
1-Biphenylene-4-phenylbutene-2	Na C_2H_5OH	(4.3%) (84.9%)	2	b.p.
1-Biphenylene-4-phenylbutene-2	Piperidine C_2H_5OH (solvent)		(long)	b.p.
1-Biphenylene-2,3-diphenylbutadiene-1,3	$CH_3 . CO_2H$ H_2SO_4	(96%?) (1%?)	1	b.p.
1,4-Dihydronaphthalene	C_2H_5ONa (10% solution)			100–105
1,4-Dihydronaphthalene	C_2H_5ONa (5% solution)			140–150
1,4-Dihydronaphthalene	C_2H_5ONa (approx. 10% solution)		3–4	150
1-Methylnaphthalene	Silica gel			420
1-Ethylnaphthalene	Silica gel			420–430
1-Methylene-2-methyl-1,4-dihydronaphthalene	HCl $CH_3 . CO_2H$	(78.5%)	4	b.p.
1,6-Dimethylnaphthalene	Silica gel			400–420
1-Allylnaphthalene	Activated Al_2O_3			500–550
1-Allylnaphthalene	Al_2O_3		(long)	300
1-Allylnaphthalene	KOH C_2H_5OH			b.p.
1-Isopropenyl-1,2,3,4-tetrahydronaphthalene	C_2H_5ONa C_2H_5OH (solvent)		8	140–150
1-Phenylnaphthalene	Silica gel Cobalt silicate			350

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes)—*Continued*

Pressure (atms.)	Products (Per cent by weight on original condensed aromatic) Isomers	Other Products	References
1	Equilibrium mixture of m.p. 70° containing 1-benzylidene-3-*p*-methylbenzyl-indene and 1-*p*-methylbenzylidene-3-benzyl-indene		(59)
1	Equilibrium mixture of m.p. 70° containing 1-benzylidene-3-*p*-methylbenzyl-indene and 1-*p*-methylbenzylidene-3-benzyl-indene		(59)
1	"Equilibrium mixture" of m.p. 71–73° containing 1-benzylidene-3-*p*-isopropylbenzyl-indene and 1-*p*-isopropyl-benzylidene-3-benzylindene		(59)
1	1-Diphenylmethylene-3-benzylindene		(656)
1	1,2,3-Triphenylindene (Na derivative)		(678)
bomb	No isomers	1-Methyl-1,3,3-triphenyl-indane (100%)	(332)
1 (N_2)	1,2,3,4-Dibenzo-9-phenyl-fluorene (Na derivative)		(313) (314)
1	1,2,3,4-Dibenzo-9-phenyl-fluorene (80%)		(316)
sealed tube	$\frac{\text{1-}p\text{-Tolyl-2,3-diphenylindene}}{\text{1,2-Diphenyl-3-}p\text{-tolylindene}} = 1.083$ (equilibrium mixture)		(315)
1	$\frac{\text{1-}p\text{-Tolyl-2,3-diphenylindene}}{\text{1,2-Diphenyl-3-}p\text{-tolylindene}} = 9$ (equilibrium mixture)		(315)
sealed tube	$\frac{\text{1-}p\text{-Tolyl-2,3-diphenylindene}}{\text{1,2-Diphenyl-3-}p\text{-tolylindene}} = 1.273$ (equilibrium mixture)		(315)
1	Isomer (m.p. 81–82°) (approximately 88%)		(580)
1	Isomer (m.p. 81–82°)	1-Biphenylene-4-phenyl-butene-2	(580)
1	1-Biphenylene-2-phenyl-3-methylindene (75%)		(316a)
	1,2-Dihydronaphthalene		(573)
	1,2-Dihydronaphthalene		(574)
	1,2-Dihydronaphthalene ("100%")		(530)
(N_2)	2-Methylnaphthalene (39%)		(365)
(N_2)	2-Ethylnaphthalene		(365)
1	1,2-Dimethylnaphthalene (58.2%)		(529)
	2,6-Dimethylnaphthalene (20%)	1,6-Dimethylnaphthalene	(365)
15 mm. Hg	1-Propenylnaphthalene		(185)
(CO_2)	1-Propenylnaphthalene		(342a)
1	1-Propenylnaphthalene		(585)
sealed tube	1-Isopropylidene-1,2,3,4-tetrahydronaphthalene (75%)		(299)
(air or H_2)	2-Phenylnaphthalene		(365)

Table 40. Isomerization of Condensed Aromatics (Indanes, Indenes,

Reactants: Condensed Aromatic	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Phenylnaphthalene (*Cont.*)	Copper silicate (used individually)		
1-Benzylnaphthalene			"glowing"
1-Benzylnaphthalene	Pumice	7–10 portions of 2–3 g. feed	"glowing"
1,1′-Dinaphthyl	$AlCl_3$ (11%) CS_2 (87%)		b.p.
1,2,3-Triphenylnaphthalene	Li Ether (solvent) C_2H_5OH (for demetalation)	8 days for metalation	room
1,2,3,4,4a,9,9a,10-Octahydroanthracene	MoS_2 (4.76%)	2 at then 1.5 at	340–350 360–370
1,2,3,4,5,6,7,8-Octahydroanthracene	MoS_2 (4.76%)	2	335
1,2,3,4,5,6,7,8-Octahydroanthracene	MoS_2 (4.76%)	2.4	390
1,2,3,4,5,6,7,8-Octahydroanthracene	$AlCl_3$ (4.76%)	3	70–80
9-Benzohydrylidene-10-phenyl-9,10-dihydroanthracene	Na Ether (solvent) C_2H_5OH (for demetalation)	10 weeks for replacement of H by one Na	room
1,4,9,10-Tetraphenylanthracene	$H \cdot CO_2H$ (90.9%)	3	b.p.
1,2,3,4,5,6,7,8-Octahydrophenanthrene	Ni (Raney's) (6–37%?)	2–10	130
1,2,3,4,5,6,7,8-Octahydrophenanthrene	Copper chromite (6–44%?)		180–230(?)
1,2,3,4,5,6,7,8-Octahydrophenanthrene	$AlCl_3$ (4.76%)	4	80
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene	Copper chromite (6–44%?)		180–230(?)
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene	Ni (Raney's) (6–37%?)	5	130 (?)
1,2,3,4,4a,9,10,10a-Octahydrophenanthrene	Ni (Raney's) (6–37%?)	19	130 (?)
9-Allylphenanthrene	Li (an excess) Ether (solvent) Alcohol (for demetalation)	30 for metalation	room
9-Allylphenanthrene	KOH (2.7%) C_2H_5OH (solvent) (81%)	4	b.p.
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	30% Pd+70% charcoal (6.75%)	2 at then 1 at	260–265 280–285

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original condensed aromatic) Isomers	Other Products	References
	1,11b-Dihydro-7-benz[de]-anthrene		(225)
(CO_2)	1,11b-Dihydro-7-benz[de]-anthrene (8%)	Naphthalene 1-Benzylnaphthalene	(525)
1	2,2′-Dinaphthyl		(526)
1	9-Phenyl-9,14-dihydro-dibenz[ac]-anthracene		(57a)
100 (H_2)	1,2,3,4,5,6,7,8-Octa-hydroanthracene	1,2,3,4,4a,9,9a,10-Octa-hydroanthracene	(450)
100 (H_2)	1,2,3,4,4a,9,9a,10-Octa-hydroanthracene	1,2,3,4,5,6,7,8-Octa-hydroanthracene	(450)
100 (H_2)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (34.25%)	Fraction, b.p. 260–285° (5.5%) Fraction, b.p. 285–290° (13.5%) Fraction, b.p. 295–305° (17.4%)	(453)
1	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (40–44%)	1,2,3,4,5,6,7,8-Octa-hydroanthracene (44%) Dodecahydrotriphenylene (4.4–4.6%) Yellow hydrocarbon, m.p. 320° (small %) Fraction containing (?) 1,3-bis-(4-[9-octracenyl]butyl)benzene and (?) 6-(4-[9-octanthrenyl]butyl)-1,2,3,4-tetrahydronaphthalene (4.0% total)	(528)
1	9-Benzohydryl-10-phenyl-anthracene		(44)
1	4,9,10-Triphenyl-1,9-(*o*-phenylene)-9,10-di-hydroanthracene		(640)
100–140 (N_2)	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene (3–4%)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene	(150)
100–140 (N_2)	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene	(150)
1	1,2,3,4,5,6,7,8-Octa-hydroanthracene (45%)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (45%) Dodecahydrotriphenylene, Other hydrocarbons (10%)	(528)
100–140 (N_2)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene	(150)
100–140 (N_2)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (15%)	1,2,3,4,4a,9,10,10a-Octa-hydrophenanthrene	(150)
100–140 (N_2)	1,2,3,4,5,6,7,8-Octa-hydrophenanthrene (28%)	1,2,3,4,4a,9,10,10a-Octa hydrophenanthrene (66%) Other hydrophenanthrenes (traces)	(150)
1	2,3-Dihydro-1-cyclopenta-[*l*]phenanthrene	9-Allylphenanthrene	(58)
1	9-Propenylphenanthrene (83.3%)		(47)
1	1-Butyl-2-methyl-phenanthrene		(95a)
1			

Table 40. Isomerization of Condensed Aromatics, Indanes, Indenes,

Reactants: Condensed Aromatic	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)	Contact Time (hours)	Temp. (°C.)
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	P_2O_5 (50%)	6	140
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	P_2O_5		170
1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	H_3PO_4 (prepared at 235° C.) (15.9%) $CH_3 . CO_2H$ (75.6%)	48 at 84 at	100 room
5,6,11,12-Tetraphenylnaphthacene (Rubrene)	HI (gas) Solvents for rubrene		
5,6,11,12-Tetraphenylnaphthacene (Rubrene)	HI (gas) Benzene (solvent)		
5,6,11,12-Tetraphenylnaphthacene (Rubrene)	HI S lvents		
5,6,11,12-Tetraphenylnaphthacene (Rubrene)	HI (gas) Ether	0.5	room
"Dihydrorubrene, m.p. 249–250°"	Conc. solution sodium isoamylate in isoamyl alcohol	1	heated
Dimethylrubrene	Strong acid (H_2SO_4) Benzene (solvent)		

Table 41. Isomerization of

Reactants: Aromatic-Cyclane	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)	Contact Time (hours)	Temp. (°C.)
1-Isopropyl-2-phenylcyclopropane	H_2SO_4, 90% H_2O, 10%		
"γ-Diphenyltruxane" (*cis*-form)		5	above 171
1,2,4-Triphenylcyclopentane		"aging for months"	room
1-Methyl-2,3,5-triphenylcyclopentane (liquid form)		"aging"	room
1,3-Dimethyl-2,4,5-triphenylcyclopentane (liquid form)		"aging"	room
1,2-Diphenyltetracyclohexylethane	Xylene (solvent) (98%)	10 min.	100
1,2-Diphenyltetracyclohexylethane	40%-Sodium amalgam Ether (solvent) Later, CO_2	6 (amalgam)	room

Fluorenes, Naphthalenes, Anthracenes, Phenanthrenes, Naphthacenes—*Continued*

Pressure (atms.)	Products (Per cent by weight on original condensed aromatic) Isomers	Other Products	References
1	1-Butyl-2-methyl-phenanthrene (below 16%) 12a-Methyl-1,4,4a,11,12,12a-hexahydrochrysene (53%)	1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene (below 16%)	(95a)
1	12a-Methyl-1,4,4a,11,12,12a-hexahydrochrysene		(95a)
1 1	12a-Methyl-1,4,4a,11,12,12a-hexahydrochrysene (crude, 3.5%)	1-(3-Butenyl)-2-methyl-3,4-dihydrophenanthrene	(95a)
	Pseudo-rubrene		(34)
	Pseudo-rubrene (large %)	I_2	(387)
	Pseudo-rubrene	I_2	(388)
1	Pseudo-rubrene (6.25%)	I_2 "Dihydrorubrene, m.p. 230–231°" (14.4%) "Dihydrorubrene, m.p. 249–250°" (35.0%)	(143)
1	"Dihydrorubrene, m.p. 230–231°" (100%)		(143)
	Isomer (m.p. 271–272°) Isomer (m.p. 293–294°)		(165)

Aromatic-Cyclane Hydrocarbons.

Pressure (atms.)	Products (Per cent by weight on original aromatic) Isomers	Other Products	References
1	1,1,2-Trimethylindane		(131a)
1	"α-Diphenyltruxane" (*trans*-form) (100%)		(568)
1	1,2,4-Triphenylcyclopentane (stable solid-form)		(403)
1	1-Methyl-2,3,5-triphenylcyclopentane (stable solid-form)		(1)
1	1,3-Dimethyl-2,4,5-triphenylcyclopentane (stable solid-form)		(1)
1	Isomer (m.p. 209°) (20%)		(474)
1	Isomer (m.p. 209°) (15%)	Phenyldicyclohexyl acetic acid (40%)	(474)

Table 42. Isomerization of

Reactants: Aromatic-Cyclene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1-(4-Phenylbutyl)cyclopentene-1	H_2SO_4, 90% H_2O, 10%		40–50 min.	9–10
1-(o-Biphenylyl)cyclopentene-1	$AlCl_3$ CS_2	(8%) (86%)	5	0
1-(β-1′-Naphthylethyl)cyclopentene-1	$AlCl_3$ CS_2	(8.1%) (85.1%)	24	0
1-Methyl-2-(β-1′-naphthylethyl)cyclopentene-1	$AlCl_3$ CS_2	(9.0%) (84.3%)	"overnight"	0
1-(β-9′-Phenanthrylethyl)-cyclopentene-1	$AlCl_3$ CS_2		12	room
1-(β-Phenethyl)cyclohexene-1	$AlCl_3$ CS_2		6	room
1-(β-Phenethyl)cyclohexene-1	$AlCl_3$ CS_2		18	room
1-(β-Phenethyl)cyclohexene-1	$AlCl_3$ CS_2	(9%) (85%)	24	room
1-(β-Phenethyl)cyclohexene-1	H_2SO_4			room (?)
1-(β-Phenethyl)cyclohexene-1	H_2SO_4 CH_3CO_2H	(14.9%) (77%)	1	b.p.
1-Methyl-2-benzylcyclohexene-1	$AlCl_3$ CS_2	(10.5%) (82.9%)	3 at then "overnight" at	0 room
1-Methyl-2-benzyl-4-isopropylcyclohexene-1	$AlCl_3$		5	0
1-Methyl-2-(β-phenethyl)-cyclohexene-1	$AlCl_3$ CS_2			0
1-Isopropyl-2-(β-phenethyl)-4-methylcyclohexene-1	Conc. H_2SO_4 (? Petroleum ether)			room (?)
1-(1′-Naphthyl)cyclohexene-1	$AlCl_3$ CS_2			0 (?)

Aromatic-Cyclene Hydrocarbons

Products

Per cent by weight on original olefin

Dehydro Isomers (above) — Other Products

1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene (115a)

9-Fluorylspirocyclopentane (52.5%) (26)

cis- and trans-2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (83%) (119)

May give instead: (117)

2,3-Dihydro-spiro[benzonaphthene-1,1'-cyclopentane] (27.1%)

2,3,3a,10,11,11a-Hexahydro-1-cyclopenta[a]phenanthrene (54.3%)

Possibility of some: 1,2-Dihydro-spiro[3-benz[e]indene-3,1'-cyclopentane]

3a-Methyl-2,3,3a,10,11,11a-Hexa-hydro-1-cyclopenta[a]phenanthrene (50%) (119)

Tetrahydrocyclopenteno-biphenylene (?) (49%) (49)

1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (116)

cis-1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (large %) (120)

trans-1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (small %)

Hydrindene-spirocyclohexane (smallest %)

1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (49%) (116)

1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (131)

1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (60%) (116)

9-Methyl-2,3-benzobicyclo[3.3.1]nonene-2 (70%) (116)

Table 42. Isomerization of the

Reactants: Aromatic-Cyclene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
1-Methyl-2-(1′-naphthyl)-cyclohexene-1	$AlCl_3$ CS_2	(8.9%) (84.0%)	6.5	0
1-Methyl-2-(2′-naphthyl-methyl)cyclohexene-1	$AlCl_3$ CS_2	(6.9%) (86.3%)	6	0
1-(β-1′-Naphthylethyl)-cyclohexene-1	$AlCl_3$ CS_2	(8.1%) (85.1%)	7	0
1-(β-1′-Naphthylethyl)-cyclohexene-1	$AlCl_3$ CS_2	(8.1%?) (85.1%?)		0
1-Methyl-2-(β-1′-naphthyl-ethyl)cyclohexene-1	$AlCl_3$ CS_2	(8.7%) (84.0%)	7	0
1-Methyl-2-(β-1′-naphthyl-*n*-propyl)cyclohexene-1	$AlCl_3$ CS_2	(7.6%) (85.6%)	21	0
1-Methyl-2-(β-1′-naphthyl-ethyl)-4-isopropylcyclo-hexene-1	$AlCl_3$ CS_2	(12.3%) (77.4%)	24	0
1-Methyl-2-(β-3′-ace-naphthylethyl)-cyclo-hexene-1	$AlCl_3$ CS_2	(7.0%) (85.7%)	21	0
1-(β-9′-Phenanthrylethyl)-cyclohexene-1	$AlCl_3$ CS_2	(6.9%) (86.3%)	2–3	0
1-Methyl-2-(β-9′-phen-anthrylethyl)cyclo-hexene-1	$SnCl_4$ HCl C_6H_6	(3.9%) (86.2%)	48	room
3-(β-Phenethyl)indene	$AlCl_3$ CS_2	(7.3%) (85.9%)	16	0
3-(β-Phenethyl)indene	H_2SO_4 $CH_3 . CO_2H$	(14.9%) (77%)	1	100
2-Methyl-3-(β-phenethyl)-indene	$AlCl_3$ CS_2	(7.7%) (85.7%)	3	0
2-Methyl-3-(β-1′-naphthyl-ethyl)indene	$AlCl_3$ CS_2	(8.3%) (83.3%)	3	0
2-Methyl-3-(β-1′-naphthyl-isopropyl)indene (?)	$AlCl_3$ CS_2 (solvent) 1,4-Di-1-naphthyl-2,3-dimethylbutane (impurity)	(6.9%) (86.2%)	"overnight"	2–3
2,5-Dimethyl-3-(β-1′-naphthylethyl)indene	$AlCl_3$ CS_2	(8.3%) (83.3%)	3	0
2,6-Dimethyl-3-(β-1′-naphthylethyl)indene (88.9% pure ?)	$AlCl_3$ CS_2 (solvent) 1,4-Di-1-naphthyl-butane (impurity)	(8.3%) (83.3%) (0.93%)	3	0
2,7-Dimethyl-3-(β-1′-naphthylethyl)indene	$AlCl_3$ CS_2	(8.3%) (83.3%)	3	0
3-(β-1′-Naphthylethyl)-4-methyl-7-isopropylindene	$AlCl_3$ CS_2		4	0

Aromatic-Cyclene Hydrocarbons—*Continued*

Pressure (atms)	Products (Per cent by weight on original aromatic) Isomers		Other Products	References
1	6b-Methyl-6b,7,8,9,10,-10a-hexahydrofluoranthrene	(66%?)		(121)
1	7a,8,9,10,11,11a-Hexahydro-11a-methyl-3,4-benzofluorene	(47%)		(113)
1	*cis*- and *trans*-1,2,3,4,4a,-11,12,12a-Octahydrochrysenes	(14.2%)		(117)
	7,8-Dihydrophenalyl-7-spirocyclohexane	(26.8%)		
1	*cis*-1,2,3,4,4a,11,12,12a-Octahydrochrysene	(0.92%)		(117)
	trans-1,2,3,4,4a,11,12,12a-Octahydrochrysene	(0.16%)		
	7,8-Dihydrophenalyl-7-spirocyclohexane			
1	4a-Methyl-1,2,3,4,4a,11,-12,12a-octahydrochrysene	(60%)		(115)
1	4a,11-Dimethyl-1,2,3,4,4a,-11,12,12a-octahydrochrysene	(72%)		(186)
1	2-Isopropyl-4a-methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene			(123)
1	8,9-Dihydro-2′-methylspiro[β-acenaphthindan-3,1′-cyclohexane]			(115)
1	Dihydrobenzanthrenespirocyclohexane	(58%)		(250)
1	Dihydrobenzanthrenespiromethylcyclohexane (?)	(80%)		(45)
1	5,6,6a,11a-Tetrahydrochrysofluorene	(18%)	Resins	(117)
1	5,6,6a,11a-Tetrahydrochrysofluorene	(16%)	Resins	(117)
1	5,6,6a,11a-Tetrahydro-11a-methylchrysofluorene	(82%)		(119)
1	11a-Methyl-5,6,6a,11a-tetrahydro-11-naphtho-[2,1-a]fluorene	(27.2%)		(25)
1	6,11a-Dimethyl-5,6,6a,-11a-tetrahydro-11-naphtho[2,1-a]fluorene (?)			(25)
1	8,11a-Dimethyl-5,6,6a,-11a-tetrahydro-11-naphtho[2,1-a]fluorene	(18.9%)		(25)
1	9,11a-Dimethyl-5,6,6a,-11a-tetrahydro-11-naphtho[2,1-a]fluorene	(5.0%)		(25)
1	10,11a-Dimethyl-5,6,6a,-11a-tetrahydro-11-naphtho[2,1-a]fluorene	(19.1%)		(25)
1	2,3-Dihydro-4′-isopropyl-7′-methyl-spiro[benzonaphthene-1,1′-indan]			(119)

Table 42. Isomerization of the

Reactants: Aromatic-Cyclene	Reactants: Catalyst (Per cent by weight on aromatic+catalyst)		Contact Time (hours)	Temp. (°C.)
2-Methyl-3-(β-[5,6,7,8-tetrahydro-1-naphthyl]ethyl)-indene	$AlCl_3$ CS_2	(8.3%) (83.3%)	3	0
2-Methyl-3-(β-[5,6,7,8-tetrahydro-1-naphthyl]ethyl)-indene	H_2SO_4 $CH_3 . CO_2H$			100
2,4-Dimethyl-3-(β-[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)-7-isopropylindene			3	0
2,4-Dimethyl-3-(β-[5,6,7,8-tetrahydro-1-naphthyl]-ethyl)-7-isopropylindene	H_2SO_4 $CH_3 . CO_2H$			100
1-(β-Phenethyl)-3,4-dihydronaphthalene	$AlCl_3$ CS_2	(8.4%) (84.9%)	6	0
2-(β-Phenethyl)-Δ^2-octalin	$AlCl_3$ CS_2	(8.5%) (84.8%)	4 at then "overnight" at	0 room
2-(β-Phenethyl)-*cis*-Δ^2-octalin	$AlCl_3$ CS_2	(8.5%) (84.5%)	3 at then several at	0 room
2-(β-*o*-Tolylethyl)-Δ^2-octalin	$AlCl_3$ CS_2	(9.5%) (83.8%)	"mixed" at then "overnight" at	0 room
1-(β-Phenethyl)-2-methyl-3-α-naphthindene	$AlCl_3$ CS_2	(6.9%) (86.3%)	4	0
1,2-Dihydro-4-(β-phenethyl)-phenanthrene	$AlCl_3$ CS_2	(12.8%) (80.8%)	12	0
1-(β-Phenethyl)-3,4-dihydrophenanthrene	$AlCl_3$ CS_2	(6.9%) (86.3%)	0.5 at then "overnight" at	0 5
1-(β-*o*-tolylethyl)-3,4-dihydrophenanthrene	$AlCl_3$ CS_2			0 (?)
1-(β-*p*-tolylethyl)-3,4-dihydrophenanthrene	$AlCl_3$ CS_2			0 (?)

Aromatic Cycloid Hydrocarbons—Continued

Products	
Isomer (ref.)	Other Products (% by weight on original)
(619)	1,2,3,4,5,6,6a,11a-Octahydro-11a-methyl-11-naphtho[2,1-a]fluorene (80%)
(619)	1,2,3,4,5,6,6a,11a-Octahydro-11a-methyl-11-naphtho[2,1-a]fluorene
(619)	1,2,3,4,5,6,6a,11a-Octahydro-7,11a-dimethyl-10-isopropyl-11-naphtho[2,1-a]fluorene (75%)
(619)	1,2,3,4,5,6,6a,11a-Octahydro-7,11a-dimethyl-10-isopropyl-11-naphtho[2,1-a]fluorene
(417)	4b,5,6,10b-… (1-Phenylethyl)-naphthalene (0.5%); Hexahydrochrysene (53.2%)
(417)	Dodecahydro-1,2-benzanthracene (34.9%)
(423)	Dodecahydro-1,2-benzanthracene (83%)
(424)	4′-Methyl-dodecahydro-1,2-benzanthracene (7.1%)
(425)	5,6,6a,13a-Tetrahydro-13a-methyldibenzo[a,g]fluorene (60%)
(416)	Hexahydro-1,2,5,6-dibenzphenanthrene (61.5%)
(416)	5,6,6a,13,14,14a-Hexahydropicene (1%)
	3′,4′-Dihydro-spiro[indan-1,1′(2′)-phenanthrene](?) (77.3%)
(414)	4-Methyl-3′,4′-dihydro-spiro[indan-1,1′(2′)phenanthrene] (?); 4-Methyl-5,6,6a,13,14,14a-hexahydropicene (?) (total 77.3%)
(414)	6-Methyl-3′,4′-dihydro-spiro[indan-1,1′(2′)phenanthrene] (?); 6-Methyl-5,6,6a,13,14,14a-hexahydropicene (?)

Table 43. Isomerization of [illegible]

Reactants

[illegible]

Aromatic-Cyclodiene Hydrocarbons

Products	
Per cent by weight on original adduct	
Pressure (atm.)	Other Products
	1,2-Dimethyl-3,4,[illegible],10,10a-hexahydrophenanthrene (82.5%)
	1-Methyl-2-phenyl-4-isopropylbenzene ([illegible])
	1-Methyl-2-phenyl-4-isopropylbenzene ([illegible])
	1-Methyl-2-benzyl-4-isopropylbenzene ([illegible])
	1-Methyl-2-benzyl-4-isopropylbenzene ([illegible])

Table 44. Possibilities of Hydrocarbon Isomerization as Illustrated by the Known Examples to Date.

("*Iso*" denotes a branched structure)

1. *n*-Alkane → *Iso*-alkane with shorter chain
2. *n*-Alkane → 2-Methylalkane with shorter chain
3. *n*-Alkane → 3-Methylalkane with shorter chain
4. *n*-Alkane → 2,4-Dimethylalkane with shorter chain
5. *n*-Alkane → 3,3-Dimethylalkane with shorter chain
6. *n*-Alkane → 2,2,3-Trimethylalkane with shorter chain
7. *Iso*-alkane → *n*-Alkane with longer chain
8. 2-Methylalkane → *n*-Alkane with longer chain
9. 2-Methylalkane → 3-Methylalkane
10. 2-Methylalkane → 2,3-Dimethylalkane with shorter chain
11. 3-Methylalkane → 2-Methylalkane
12. 2,2-Dimethylalkane → 2-Methylalkane with longer chain
13. 2,2-Dimethylalkane → 2,3-Dimethylalkane
14. 2,3-Dimethylalkane → 2-Methylalkane with longer chain
15. 2,3-Dimethylalkane → 2,2-Dimethylalkane
16. 2,4-Dimethylalkane → 2,3-Dimethylalkane
17. *n*-Alkene → Geometrical isomer (*cis* or *trans*)
18. *n*-Alkene → *n*-Alkene with shifted double-bond
19. *n*-Alkene → *Iso*-alkene
20. *n*-Alkene → Cyclane
21. *Iso*-alkene → *Iso*-alkene with shifted double-bond
22. 2-Methylalkene-1 → 3-Methylalkene-1
23. 2-Methylalkene-1 → 2-Methylalkene-2
24. 3-Methylalkene-1 → 2-Methylalkene-1
25. 3-Methylalkene-1 → 2-Methylalkene-2
26. 2-Methylalkene-2 → 2-Methylalkene-1
27. 2-Methylalkene-2 → 3-Methylalkene-1
28. 3-Methylalkene-2 → 2-Ethylalkene-1 by shift of double-bond only
29. 2-Ethylalkene-1 → 3-Methylalkene-2 by shift of double-bond only
30. 2,3-Dimethylalkene-1 → 2,3-Dimethylalkene-2
31. 2,3-Dimethylalkene-2 → 2,3-Dimethylalkene-1
32. *Iso*-alkene → *Iso*-alkene with shifted methyl-group
33. 2,3-Dimethylalkene-1 → 3,3-Dimethylalkene-1
34. *Iso*-alkene → *Iso*-alkene with shifted double-bond and shifted methyl-group
35. 3-Methylalkene-2 → 2-Methylalkene-1
36. 2,3-Dimethylalkene-2 → 3,3-Dimethylalkene-1
37. *Iso*-alkene → Alkyl cyclane
38. Non-allenic, unconjugated *n*-alkadiene → Conjugated *n*-alkadiene by shift of one double-bond only
39. Non-allenic, unconjugated *n*-alkadiene → Conjugated *n*-alkadiene by shift of both double-bonds
40. Non-allenic, unconjugated *n*-alkadiene → Non-allenic, unconjugated *iso*-alkadiene with shorter chain
41. Non-allenic, unconjugated *n*-alkadiene → *n*-Alkyne
42. Non-allenic, conjugated *n*-alkadiene → Non-allenic, unconjugated *n*-alkadiene
43. Non-allenic, conjugated *n*-alkadiene → Conjugated *n*-alkadiene
44. Non-allenic, unconjugated *iso*-alkadiene → Non-allenic, unconjugated *iso*-alkadiene by shift of one double-bond only
45. Non-allenic, unconjugated *iso*-alkadiene → Conjugated *iso*-alkadiene by shift of one double-bond only
46. Non-allenic, unconjugated *iso*-alkadiene → Conjugated *iso*-alkadiene by shift of both double-bonds
47. Non-allenic, unconjugated *iso*-alkadiene → Polyalkyl cyclene
48. Non-allenic, conjugated *iso*-alkadiene → *Iso*-allenic
49. *n*-Allenic → Conjugated *n*-alkadiene

Table 44—*Continued*

50. *n*-Allenic → *n*-Alkyne
51. *Iso*-allenic → Conjugated *iso*-alkadiene
52. *Iso*-allenic → Conjugated *iso*-alkadiene with shifted methyl-group
53. *Iso*-allenic → *Iso*-alkyne
54. *Iso*-alkatriene-1,2,3 → *Iso*-alken-3-yne-1
55. *Iso*-alkapolyene → Less-conjugated *iso*-alkapolyene
56. *Iso*-alkapolyene → More-conjugated *iso*-alkapolyene
57. Partly - conjugated *iso*-alkapolyene → Conjugated polyalkyl - monoalkylidene cyclene
58. Partly-conjugated *iso*-alkapolyene → Polyalkyl hexahydronaphthalene
59. Partly - conjugated *iso* - alkapolyene → Unconjugated polyalkyl - monoalkenyl cyclene
60. Partly - conjugated *iso*-alkapolyene → "Unconjugated" alkyl-*iso*alkadienyl cyclene
61. Unconjugated *iso*-alkapolyene → "Unconjugated" polyalkyl-monoalkenyl cyclene
62. *n*-Alkyne → *n*-Alkyne with shifted triple-bond
63. *n*-Alkyne → *n*-Allenic
64. *n*-Alkyne → Non-allenic, conjugated *n*-alkadiene
65. *Iso*-alkyne → Conjugated *iso*-alkadiene
66. *Iso*-alkyne → *Iso*-allenic
67. Unconjugated *n*-alkadiyne → Conjugated *n*-alkadiyne
68. Unconjugated *iso*-alkapolyyne → Conjugated *iso*-alkapolyenepolyyne
69. *n*-Cyclane → *n*-Alkene
70. *n*-Cyclane → Alkyl cyclane of smaller ring-size
71. Alkyl cyclane → *n*-Alkene
72. Alkyl cyclane → *Iso*-alkene
73. Alkyl cyclane → Polyalkyl cyclane of smaller ring-size
74. Alkyl cyclane → Stable multiplanar-form with "same" ring-size
75. Alkyl cyclane → Polyalkyl cyclane with same ring-size
76. *Iso*alkyl cyclane → Polyalkyl cyclane with same ring-size
77. Alkylcyclane → Alkyl cyclane of larger ring-size but with smaller alkyl
78. Alkyl cyclane → Polyalkyl cyclane of larger ring-size but with smaller alkyls
79. Alkyl cyclane → *n*-Cyclane of larger ring-size
80. Dialkyl cyclane → Polyalkyl cyclane with smaller alkyls
81. Dialkyl cyclane → Alkyl cyclane of larger ring-size
82. Polyalkyl cyclane → Stable geometrical-form with same ring-size
83. Polyalkyl cyclane → Polyalkyl cyclane of same ring-size but *ortho*-resubstituted
84. Polyalkyl cyclane → Polyalkyl cyclane of same ring-size but *meta*-resubstituted
85. Polyalkyl cyclane → Polyalkyl cyclane of same ring-size but *para*-resubstituted
86. Alkenyl cyclane → Alkenyl cyclane with shifted double-bond
87. Alkenyl cyclane → Conjugated *n*-alkadiene
88. Alkenyl cyclane → Conjugated *iso*-alkadiene
89. Alkenyl cyclane → Alkyl cyclene
90. *Iso*alkenyl cyclane → *Iso*alkyl cyclene
91. Alkyl-*iso*alkenyl cyclane → Alkyl-*iso*alkyl cyclene
92. Alkadienyl cyclane → Alkynyl cyclane
93. Alkadienyl cyclane → Alkenyl cyclene
94. Alkynyl cyclane → Alkynyl cyclane with shifted triple-bond
95. Alkynyl cyclane → Alkadienyl cyclane
96. Dicyclanyl → Form with "same" ring-sizes but different stability
97. Spirane → Bicyclane
98. *n*-Bicyclane → Stable (*trans*) form with same ring-sizes
99. *n*-Bicyclane → Polyalkyl bicyclane with both rings smaller
100. *n*-Bicyclane → *n*-Bicyclane with one ring larger
101. Alkyl bicyclane → Stable (*trans*) form with same ring-sizes
102. Alkyl bicyclane → Polyalkyl bicyclane with one ring smaller
103. Alkyl-alkenyl bicyclane → Polyalkyl-monoalkenyl cyclene
104. Alkyl-alkenyl bicyclane → Polyalkyl cyclodiene
105. Polyalkyl-monoalkenyl bicyclane → *Iso*-alkatriene
106. Polyalkyl-monoalkenyl bicyclane → Alkyl-*iso*alkenylcyclene with new alkyl
107. Polyalkyl-monoalkenyl bicyclane → Polyalkyl cyclodiene with new alkyls

Table 44—*Continued*

108. Polyalkyl-monoalkenyl bicyclane → Polyalkyl-monoalkenyl bicyclane *via* Wagner rearrangement
109. Polyalkyl-monoalkenyl bicyclane → Polyalkyl bicyclene with one more alkyl
110. Polyalkyl-monoalkenyl bicyclane → Polyalkyl bicyclene with one more alkyl, *via* Wagner rearrangement
111. Polyalkyl-monoalkenyl bicyclane → Polyalkyl bicyclene with different ring-sizes and one more alkyl
112. Tricyclane → Stable (*trans*) form with same ring-sizes and same ring-attachment
113. Tricyclane → Labile (*cis*) form with same ring-sizes and same ring-attachment
114. Tricyclane → Tricyclane with same ring-sizes and different ring-attachment
115. Polyalkyl tricyclane → Polyalkyl-monoalkenyl bicyclane with loss of one alkyl
116. Polyalkyl tricyclane → Polyalkyl bicyclene
117. Polyalkyl tricyclane → Polyalkyl bicyclene with a shifted alkyl-group
118. Alkyl cyclene → Conjugated *n*-alkadiene
119. Alkyl cyclene → Alkylidene cyclane
120. Polyalkyl cyclene → Polyalkyl cyclene with shifted double-bond
121. Partly-conjugated alkyl-*iso*alkapolyenyl cyclene → "Unconjugated" polyalkyl-*iso*alkyl bicyclodiene
122. Unconjugated alkenyl cyclene → Conjugated alkenyl cyclene
123. Alkenyl cyclene → *n*-Bicyclene with removal of side-chain double-bond
124. Alkenyl cyclene → *n*-Bicyclene with removal of ring double-bond
125. Alkyl-alkenyl cyclene → Alkyl bicyclene with removal of ring double-bond and shift of the other double bond
126. *d*-Rotatory alkyl-*iso*alkenyl cyclene → *Racemic* alkyl-*iso*alkenyl cyclene
127. Alkyl-*iso*alkenyl cyclene → Alkyl-*iso*alkenyl cyclene with shifted double-bond in side-chain
128. Alkyl-*iso*alkenyl cyclene→Alkyl-*iso*alkenyl cyclene with shifted double-bond in ring
129. Alkyl-*iso*alkenyl cyclene → Alkyl-*iso*alkyl cyclodiene
130. *Iso*alkenyl-*iso*alkapolyenyl cyclene → Polyalkyl-*iso*alkenyl bicyclene
131. Polyalkyl-*iso*alkapolyenyl cyclene → More-conjugated polyalkyl-*iso*alkapolyenyl cyclene
132. Polyalkyl-*iso*alkapolyenyl cyclene → Less-conjugated polyalkyl-*iso*alkapolyenyl cyclene
133. Alkynyl cyclene → Alkyl benzene
134. Polyalkyl cyclodiene → Polyalkyl cyclodiene with one shifted double-bond in ring
135. Polyalkyl-monoalkenyl cyclodiene → Polyalkyl benzene
136. *n*-Bicyclene → *n*-Bicyclene with shifted double-bond
137. Polyalkyl bicyclene → Conjugated *iso*-alkapolyene
138. Polyalkyl bicyclene → Alkyl-*iso*alkenyl cyclene
139. Polyalkyl bicyclene → Conjugated polyalkyl cyclodiene
140. Polyalkyl bicyclene → Polyalkyl-monoalkenyl bicyclane *via* double Wagner-rearrangement
141. *n*-Tricyclene → *n*-Tricyclene with shifted double-bond
142. Polyalkyl tricyclene → Polyalkyl bicyclodiene
143. Polyalkyl tricyclene → Bicyclic isomer
144. Polyalkyl tricyclene → Tricyclic isomer
145. Polyalkyl-(*iso*?)alkenyl tricyclene → Polyalkyl tetracyclene
146. Polyalkyl tetracyclodiene → Polyalkyl tetracyclodiene with shifted double-bonds
147. Polyalkyl pentacyclene → Polyalkyl pentacyclene with shifted double-bond
148. Aliphatic sesquiterpene → Monocyclic sesquiterpene
149. Aliphatic sesquiterpene → Bicyclic sesquiterpene
150. Monocyclic sesquiterpene → Bicyclic sesquiterpene
151. Bicyclic sesquiterpene → Monocyclic sesquiterpene
152. Bicyclic sesquiterpene → Isomeric bicyclic sesquiterpene
153. Bicyclic sesquiterpene → Tricyclic sesquiterpene
154. Tricyclic sesquiterpene → Bicyclic sesquiterpene
155. Monocyclic diterpene → Bicyclic diterpene
156. Bicyclic diterpene → Tricyclic diterpene
157. Tricyclic diterpene → Tetracyclic diterpene
158. Tetracyclic diterpene → Isomeric tetracyclic diterpene
159. Alkyl benzene → Alkenyl cyclodiene

Table 44—*Continued*

160. Alkyl benzene → Polyalkyl benzene
161. Polyalkyl benzene → Polyalkyl benzene with *ortho* resubstitution
162. Polyalkyl benzene → Polyalkyl benzene with *meta* resubstitution
163. Polyalkyl benzene → Polyalkyl benzene with *meta* resubstitution and formation of "secondaried" alkyl
164. Polyalkyl benzene → Polyalkyl benzene with *meta* resubstitution and formation of "tertiaried" alkyl
165. Polyalkyl benzene → Polyalkyl benzene with *para* resubstitution
166. Hexaphenylethane → *p*-Benzohydryltetraphenylmethane
167. *Racemic*-1,2-dialkyl-1,2-diaryl ethane → *Meso*-1,2-dialkyl-1,2-diaryl ethane
168. *Meso*-1,2-dialkyl-1,2-diaryl ethane → *Racemic*-1,2-dialkyl-1,2-diaryl ethane
169. Alkenyl benzene → Alkenyl benzene with shifted double-bond

170. Alkenyl benzene → Alkyl tetralin
171. *Iso*alkenyl benzene → Polyalkyl indane
172. Alkyl-alkenyl benzene → Alkyl-alkenyl benzene with shifted double-bond
173. Dialkenyl benzene → Dialkenyl benzene with one shifted double-bond
174. Dialkenyl benzene → Dialkenyl benzene with two shifted double-bonds
175. Diphenylethylene → Geometrical isomer (*cis* or *trans*)
176. Phenyl-(*o*-biphenylyl)-ethylene → Phenyldihydrophenanthrene
177. Polyaryl propene → Polyaryl propene with shifted double-bond
178. Polyaryl propene → Polyaryl indane
179. Polyaryl propene → Polyaryl indane with shifted phenyl-group

180. Polyaryl butene → Stable form
181. Polyaryl butene → Polyaryl butene with shifted double-bond
182. Polyaryl butene → Polyaryl butene with shifted double-bond and two shifted phenyl-groups
183. Polyaryl butene → Polyaryl cyclobutane
184. Polyaryl butene → Alkyl-polyaryl indane
185. Polyaryl butene → Aralkyl-polyaryl indane
186. Alkyl-diaryl pentene → Polyalkyl-monoaryl indane
187. Alkadienyl benzene → Stable form
188. Alkadienyl benzene → Alkynyl benzene
189. Diaryl butadiene → Stable form

190. Polyaryl butadiene → Arylmethylene-polyaryl indane
191. Polyaryl butadiene → 1-Arylmethyl-polyaryl indene
192. Polyaryl butadiene → 1-Methyl-polyaryl indene
193. Diaryl-biphenylene butadiene → Methyl-aryl-biphenylene indene
194. *d*-Rotatory polyaryl allene → *Racemic* polyaryl allene
195. Polyaryl allene → Polyaryl indene
196. Polyaryl allene → Polyaryl 3-α-naphthindene
197. Polyalkyl-polyaryl diallenic → Polyalkyl-polyaryl biindene
198. Polyaryl alkapolyene → Stable form
199. *ar*-Conjugated polyaryl trivinylmethane → *ac*-Conjugated isomer

200. Alkynyl benzene → Alkadienyl benzene
201. Alkynyl benzene → Alkynyl benzene with shifted triple-bond
202. Polyaryl alkyne-2 → Polyaryl alkadiene-1,3
203. Polyaryl unconjugated-alkadiyne → Stable isomer
204. Polyaryl unconjugated-*polyiso*-alkadiyne → Stable isomer
205. Polyaryl unconjugated-*polyiso*-alkadiyne → Polyaryl conjugated-*polyiso*-alkapolyene
206. 1-*Iso*alkenylidene indene → Polyalkyl dihydrofluorene
207. 1-Aryl indene → 3-Aryl indene
208. 3-Aryl indene → 2-Aryl indene
209. 1-Aryl-3-*iso*alkyl indene → 1-*Iso*alkyl-3-aryl indene

210. 1,2-Diaryl indene → 3,2-Diaryl indene
211. 1-(A-Arylmethylene)-3-(B-arylmethyl)indene → 1-(B-Arylmethylene)-3-(A-arylmethyl) indene
212. 1,1,3-Triaryl indene → 1,2,3-Triaryl indene
213. 1,2,3-Triaryl indene → 3,2,1-Triaryl indene
214. 1-Diphenylmethylene-indene → 3-Benzhydrylindene
215. 1,3-Dibenzylidene-indane → 1-Benzylidene-3-benzylindene

Table 44—*Continued*

216. 1,4-Dihydronaphthalene → 1,2-Dihydronaphthalene
217. 1-Alkylnaphthalene → 2-Alkyl naphthalene
218. 1-Alkylidene-2-alkyl-1,4-dihydronaphthalene → 1,2-Dialkyl naphthalene
219. 1,6-Dialkyl naphthalene → 2,6-Dialkyl naphthalene
220. 1-Alkenyl naphthalene → 1-Alkenyl naphthalene with shifted double-bond in side-chain
221. 1-*Iso*alkenyl-1,2,3,4-tetrahydronaphthalene → 1-*Iso*alkylidene-1,2,3,4-tetrahydronaphthalene
222. 1-Aryl naphthalene → 2-Aryl naphthalene
223. 1-Benzyl naphthalene → Dihydrobenzanthrene
224. 1,2,3-Triaryl naphthalene → 9-Aryl-9,14-dihydro-dibenz[ac]anthracene
225. *unsym.*-Octahydroanthracene → *sym.*-Octahydroanthracene
226. *sym.*-Octahydroanthracene → *unsym.*-Octahydroanthracene
227. *sym.*-Octahydroanthracene → *sym*-Octahydrophenanthrene
228. Polyaryl anthracene → Polyaryl 1,9-(*o*-phenylene)-9,10-dihydroanthracene with "loss" of one aryl-group
229. Aryl-9-diphenylmethylene 9,10-dihydroanthracene → Aryl-9-diphenylmethyl anthracene with "gain" of one aryl-ring
230. *unsym.*–Octahydrophenanthrene → *sym.*-Octahydrophenanthrene
231. *sym.*-Octahydrophenanthrene → *sym.*-Octahydroanthracene
232. *sym.*-Octahydrophenanthrene → *unsym.*-Octahydrophenanthrene
233. 9-Alkenyl phenanthrene → 9-Alkenyl phenanthrene with shifted double-bond in side-chain
234. 9-(Alk-2-enyl)phenanthrene → 2,3-Dihydro-1-cyclopenta[l]phenanthrene
235. Alkyl-alkenyl dihydrophenanthrene → Dialkyl phenanthrene
236. Alkyl-1-(alk-3-enyl) dihydrophenanthrene → Alkyl hexahydrochrysene
237. Polyaryl naphthacene → Phenylene isomers with less arylation
238. Poly-cyclohexyl-and-polyaryl ethane → Stable isomer with rearrangement of structure
239. *Iso*alkyl-aryl cyclane → Polyalkyl indane
240. Polyaryl cyclane → Stable form
241. Alkyl-polyaryl cyclane → Stable form
242. Polyalkyl-polyaryl cyclane → Stable form
243. Polyalkyl-polyaryl cyclane of condensed (dehydrogenated) type → Stable form
244. (4-Phenylbutyl)cyclopentene → 1-Cyclopentyl-1,2,3,4-tetrahydronaphthalene
245. *o*-Biphenylyl cyclopentene → Tetracyclic spirane
246. β-1′-Naphthylethyl cyclopentene → Hexahydro-1-cyclopenta[a]phenanthrene
247. Alkyl-β-1′-naphthylethyl cyclopentene → Alkyl hexahydro-1-cyclopenta[a]phenanthrene
248. β-9′-Phenanthrylethyl cyclopentene → Tetrahydrocyclopentenotriphenylene
249. Alkyl-benzyl cyclohexene → Alkyl 2,3-benzbicyclo[3.3.1]nonene-2
250. Polyalkyl-benzyl cyclohexene → Polyalkyl 2,3-benzbicyclo[3.3.1]nonene-2
251. β-Phenethyl cyclohexene → *unsym.*-Octahydrophenanthrenes
252. β-Phenethyl cyclohexene → Hydrindene-spirocyclohexane
253. Alkyl-β-phenethyl cyclohexene → Alkyl *unsym.*-octahydrophenanthrene
254. Polyalkyl-β-phenethyl cyclohexene → Polyalkyl *unsym.*-octahydrophenanthrene
255. Alkyl-1′-naphthyl cyclohexene → Alkyl hexahydrofluoranthene
256. Alkyl-2′-naphthylmethyl cyclohexene → Alkyl hexahydro-3,4-benzofluorene
257. β-1′-Naphthylethyl cyclohexene → Octahydrochrysene
258. β-1′-Naphthylethyl cyclohexene → Dihydro-spiro[benzonaphthene-1,1′-cyclohexane]
259. Alkyl-β-1′-naphthylethyl cyclohexene → Alkyl octahydrochrysene
260. Polyalkyl-β-1′-naphthylethyl cyclohexene → Polyalkyl octahydrochrysene
261. Alkyl-β-1′-naphthylpropyl cyclohexene → Polyalkyl octahydrochrysene
262. Alkyl-β-3′-acenaphthylethyl cyclohexene → Alkyl pentacyclic spirane
263. β-9′-Phenanthrylethyl cyclohexene → Pentacyclic spirane
264. Alkyl-β-9′-phenanthrylethyl cyclohexene → Alkyl pentacyclic spirane
265. β-Phenethyl indene → Tetrahydrochrysofluorene
266. Alkyl-β-phenethyl indene → Alkyl tetrahydrochrysofluorene
267. Alkyl-β-1′-naphthylethyl indene → Alkyl tetrahydronaphtho[2,1-a]fluorene
268. Polyalkyl-β-1′-naphthylethyl indene → Polyalkyl pentacyclic spirane

Table 44—*Continued*

[illegible]

Appendix I

The following extended translation of Moldavsky and Livschitz's fundamental work on iso-alkane determination [*J. Gen. Chem. (U. S. S. R.)*, **5,** 422-431 (1935)] is submitted by the present authors for the perusal of readers interested in the quantitative estimation of alkane isomers by means of antimony pentachloride. The basis of their method consists of an x-fold chlorination of alkane molecules.

$$C_nH_{2n+2} + xSbCl_5 \longrightarrow C_nH_{2n+2-x}Cl_x + xSbCl_3 + xHCl$$

The extent of substitution ($x=1$ to 6) depends both upon the degree of chain branching in the alkane and upon the total time of reaction. The amount of antimony trichloride formed, which is a measure of the chlorination, is determined by titration against a standard solution of potassium bromate,

$$3SbCl_3 + KBrO_3 + 6HCl \longrightarrow 3SbCl_5 + KBr + 3H_2O$$

Isomerization of Hydrocarbons. *I. The Chlorination of Hexane and Octane Isomers by Means of Antimony Pentachloride as a Quantitative Method of their Determination.* B. L. Moldavsky and S. E. Livschitz, State Institute of High Pressure.

In studies of n-hexane and n-octane isomerization, we found it necessary to develop an analytical method for small quantities of these hydrocarbons and their isomers. The present methods for iso-alkane determination are based on the large difference in reactivities of hydrogen attached to a tertiary carbon atom and hydrogen attached to primary or secondary carbon atoms. The nitration procedure of M. Konovalov should be noticed first among these methods.

This method has been used by other investigators to study the structure of petroleum hydrocarbons. Markovnikov and his pupils have conducted particularly large investigations in a study of Caucasian oils. S. Nametkin and S. Nefontova[386a] have recently applied Konovalov's method in a study of the structure of alkanes from Grozny and American sources. In spite of the big role of nitration observed by Konovalov in oil-structure studies, his method cannot be used quantitatively. It is an objectionably incomplete nitration that always leaves a large amount of unreacted hydrocarbons.

Among the different attempts to determine iso-structure hydrocarbons, most attention probably should be given to Schaarschmidt's method[500, 500a, 574d] of chlorination by $SbCl_5$. The ability of antimony pentachloride to chlorinate organic compounds has been known a long time, and it is used for such purposes in many cases.[257b]

V. Meyer and F. Müller[375a] studied chlorination by $SbCl_5$ in the aliphatic series. By using equimolecular quantities of polyhalogen derivatives of the methane series hydrocarbons (C_2H_6, C_3H_8, C_4H_{10}) and $SbCl_5$, they found that the second halogen is always placed in proximity to the first. Schaarschmidt studied the action of $SbCl_5$ on alkanes and "naphthenes." His experiments have demonstrated that the *n*-alkanes, the "naphthenes" without side-chains, and iso-compounds with quaternary carbon atoms are chlorinated very slowly at room temperature and rapidly only at temperatures above 60°. But the iso-alkanes and the "naphthenes" with side-chains, *i.e.*, the compounds containing hydrogen at a tertiary carbon atom, are rapidly chlorinated by $SbCl_5$ at room temperature and even at 0° According to this author, it is possible to recognize 0.1 per cent of iso-compounds in *n*-alkanes by means of $SbCl_5$. Obviously, the material to be investigated must not contain any alkenes or aromatic hydrocarbons, which are easily chlorinated by $SbCl_5$. The action of $SbCl_5$ on iso-compounds gives colorless or slightly yellow crystalline precipitates, which contain two molecules of $SbCl_5$ for one of the iso-compound. His experiments on the chlorination of iso- and *n*-alkanes have shown that an induced chlorination of the latter occurs and seriously interferes with the quantitative analysis.

Deciding to use Schaarschmidt's method for the analysis of mixtures of isomeric hexanes and octanes, we started a study of the chlorination effected by $SbCl_5$. The serious difficulties of Schaarschmidt's method are, first, induced chlorination of *n*-alkanes and, secondly, the absence of a quantitative check on the course of the chlorination. Therefore, it was decided to conduct this reaction in the presence of solvents and to control the amount of $SbCl_5$ used in the chlorination. Since $SbCl_3$ is formed during chlorination of the hydrocarbons, a determination of either the $SbCl_5$ used or $SbCl_3$ formed gives the extent of iso-compound chlorination. We used the iodometric method of Szebellédy[575b] in order to determine the $SbCl_5$, and that of Györy[590a] for $SbCl_3$. The methods of determination of $SbCl_5$ and $SbCl_3$ gave satisfactory results when conducted in water, chloroform, or carbon tetrachloride solution.

Materials Used and Method of Operation

The following hydrocarbons were synthesized: 2-methylbutane, *n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, *n*-octane, 4-methylheptane, and 2,5-dimethylhexane. With the exception of 2,5-dimethylhexane, all iso-compounds were prepared by reduction of our synthesized, corresponding tertiary alcohols with hydrogen under pressure and MoS_2 as catalyst.[380a] The *n*-hexane, *n*-octane, and 2,5-dimethylhexane were prepared by the Würtz reaction. The resulting *n*-alkanes contained a small amount of isomers due probably to the presence of these isomers in the original *n*-propyl and butyl alcohols. In order to remove such isomers, the *n*-alkanes were treated with 10 weight-per cent of $SbCl_5$ for 2-3 hours at room temperature, washed with alkali and water, dried, and distilled over metallic sodium. Iso-compounds obtained by the reduction of tertiary alcohols were treated several times with sulfuric acid (sp. gr. 1.84), washed with alkali and water, and also distilled over sodium. The synthesized hydrocarbons had the following boiling points: 2-methylbutane 29-31.5°, 2-methylpentane 60-61°, 3-

methylpentane 62-63°, 2,3-dimethylbutane 57-58.5°, n-hexane 68-69°, 4-methylheptane 117-118.5°, 2,5-dimethylhexane 108-109°, and n-octane 125-127°.

The following methods were used in the experiments. Carefully cleaned test tubes were placed in a large vessel containing snow or ice. One ml. of $SbCl_5$ solution in CCl_4 or $CHCl_3$ and of various concentrations was placed in the carefully cleaned and dried test tubes by means of a pipette. The concentration of $SbCl_5$ was determined by titration according to Szebellédy's method. The test tubes were closed by rubber stoppers supplied with capillary tubing. After standing in snow for 5 minutes, 0.1-0.2 ml. of 0.5-2.0N solution of iso-compound in chloroform or carbon tetrachloride was added to the test tubes by means of a micropipette. After a certain time, a white crystalline precipitate began to form in the test tubes and the solution started to turn brown in color. After a predetermined interval of time, the content of each test tube was decomposed by 3 ml. of alcohol, followed by 10 ml. of hydrochloric acid (sp. gr. 1.19), and then poured into a glass flask containing 60 ml. of water. Alcohol addition is recommended for the decomposition procedure on account of the easy solubility of the precipitated complex in alcohol, forming a violet-colored solution. This makes it easy to follow the course of the hydrolysis of the complex. After adding 2-3 drops of methyl orange indicator, the solution is titrated with 0.1N solution of $KBrO_3$, and the amount of $SbCl_3$ is calculated for one mole of iso-compound. The amount of $SbCl_3$ in the original solution must be determined before every experiment, since the $SbCl_5$ solution changes its factor upon standing and increases its content of $SbCl_3$.

The Action of $SbCl_5$ on n-Hexane and Its Isomers

The influence of the solvent on the speed of chlorination: The first experiments were carried out in carbon tetrachloride solution. It was necessary to use very strong solutions of $SbCl_5$; otherwise the chlorination proceeded very slowly. The reaction goes much faster when $CHCl_3$ is used as solvent. The experimental results are given in Table 1.

Table 1.

Conc. of $SbCl_5$ Solution	Hydrocarbon	Number of Molecules of $SbCl_3$ Formed per 1 Molecule of Iso-compound — in CCl_4 after 1 hour	in CCl_4 after 3 hours	in $CHCl_3$ after 1 hour	in $CHCl_3$ after 3 hours
3 N	2-Methylbutane	0.15	0.40	3.1	3.8
2.25 N	2,3-Dimethylbutane	0.40	0.80	..	..
2.25 N	2-Methylpentane	2.5	3.3	..	..
2 N	2,3-Dimethylbutane	..	..	3.0	3.3
2 N	2-Methylpentane	1.5	1.7	3.3	3.6
1 N	2,3-Dimethylbutane	..	..	2.5	2.7
1 N	2-Methylpentane	..	1.0	2.8	3.0

For comparison, we give also the data obtained on isopentane (2-methylbutane). In every experiment, 1 ml. of $SbCl_5$ solution and 0.1 ml. of 2*N* solution of the iso-compound were used.

Role of $SbCl_5$ concentration and the degree of chlorination of isomeric hexanes: The experiments were conducted in chloroform solution. Figure 1 shows the influence of $SbCl_5$ concentration. From this figure, it can be seen that the initial chlorination occurs very rapidly and to an extent which depends upon the concentration of the $SbCl_5$ solution. Thereafter, the chlorination very suddenly slows down. All the Figure 1

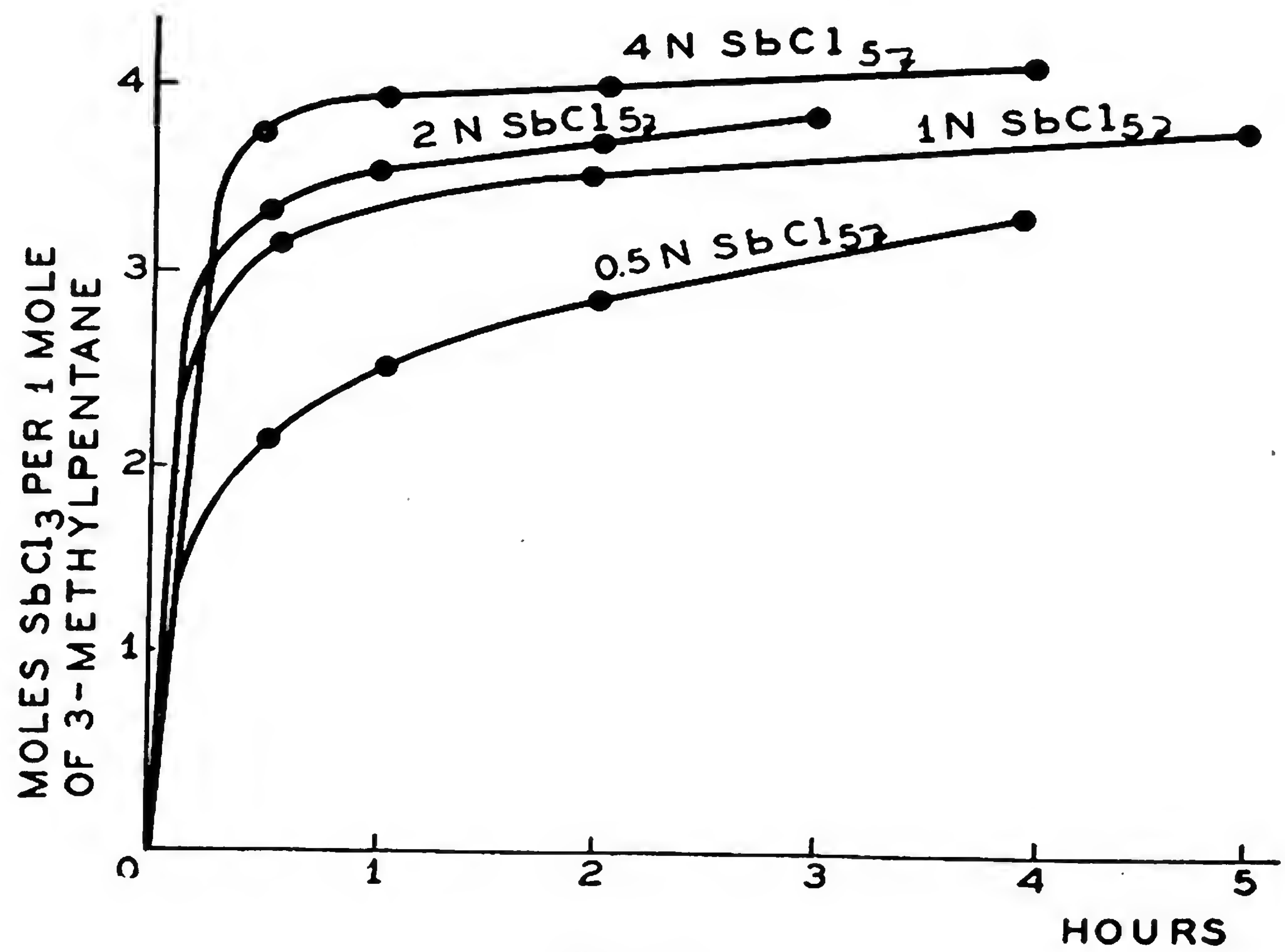


FIG. 1.

experiments were conducted with an excess of $SbCl_5$ (20 moles per one mole of iso-compound). Special experiments were made to see if *n*-hexane chlorinates in the presence of its isomers. Experiments with 2*N* $SbCl_5$ solution have shown that hexane itself does not react at room temperature even after 18 hours. With the mixture of isomers, a slight chlorination of *n*-hexane was observed with 1-1.5*N* solutions of $SbCl_5$. Experiments were conducted with an even more dilute solution of $SbCl_5$ (0.5*N*) in order to avoid chlorination of *n*-hexane. In the work with these solutions, it was observed that the reaction does not always begin with the same high velocity, since long standing is necessary in some cases, and even heating does not start the reaction in other examples. After several unsuccessful attempts, it was noticed that moisture has a very substantial influence on the reaction.

Influence of moisture on the activity of $SbCl_5$ solutions: The chlorination with very dilute solution of $SbCl_5$ (0.2-0.25*N*), if previously dried over P_2O_5, occurs without failure and much more energetically than

with former solutions of the same concentration. It is necessary to notice that there is no formation of a precipitate from the P_2O_5-dried solutions, whereas one is immediately formed from undried solutions. The precipitate obtained on chlorination with $SbCl_5$ is probably a complex (its titration shows that some $SbCl_3$ is present). This complex liquefies in the air and becomes violet-colored in the presence of alcohol or wet ether; an excess of the solvent causes disappearance of the color, due to hydrolysis, and precipitation of antimony acids. In order to study the influence of moisture on the precipitates, a chloroform solution of antimony pentachloride monohydrate ($SbCl_5 \cdot H_2O$) was prepared by adding the corresponding amount of water to $SbCl_5$ with cooling, and dissolving the resulting monohydrate in chloroform. The concentration of this solution was about 1*N* when saturated at room temperature. It gave voluminous crystalline precipitates on chlorinating 2- and 3-methylpentanes, but 2,3-dimethylbutane did not react. Other experiments with the $SbCl_5 \cdot H_2O$ solution were discontinued. However, detailed study of this complex will be of great interest. The difference between these precipitates obtained from chloroform solution and those described by Schaarschmidt is not clear. It is only necessary to indicate that part of the resulting $SbCl_3$ is always precipitated with the complex in the form of good crystals when working without solvent or with concentrated solutions, as observed in carbon tetrachloride solution in which $SbCl_3$ is very slightly soluble. We found that 22.4 g. of $SbCl_3$ are soluble in 100 ml. of chloroform at room temperature.

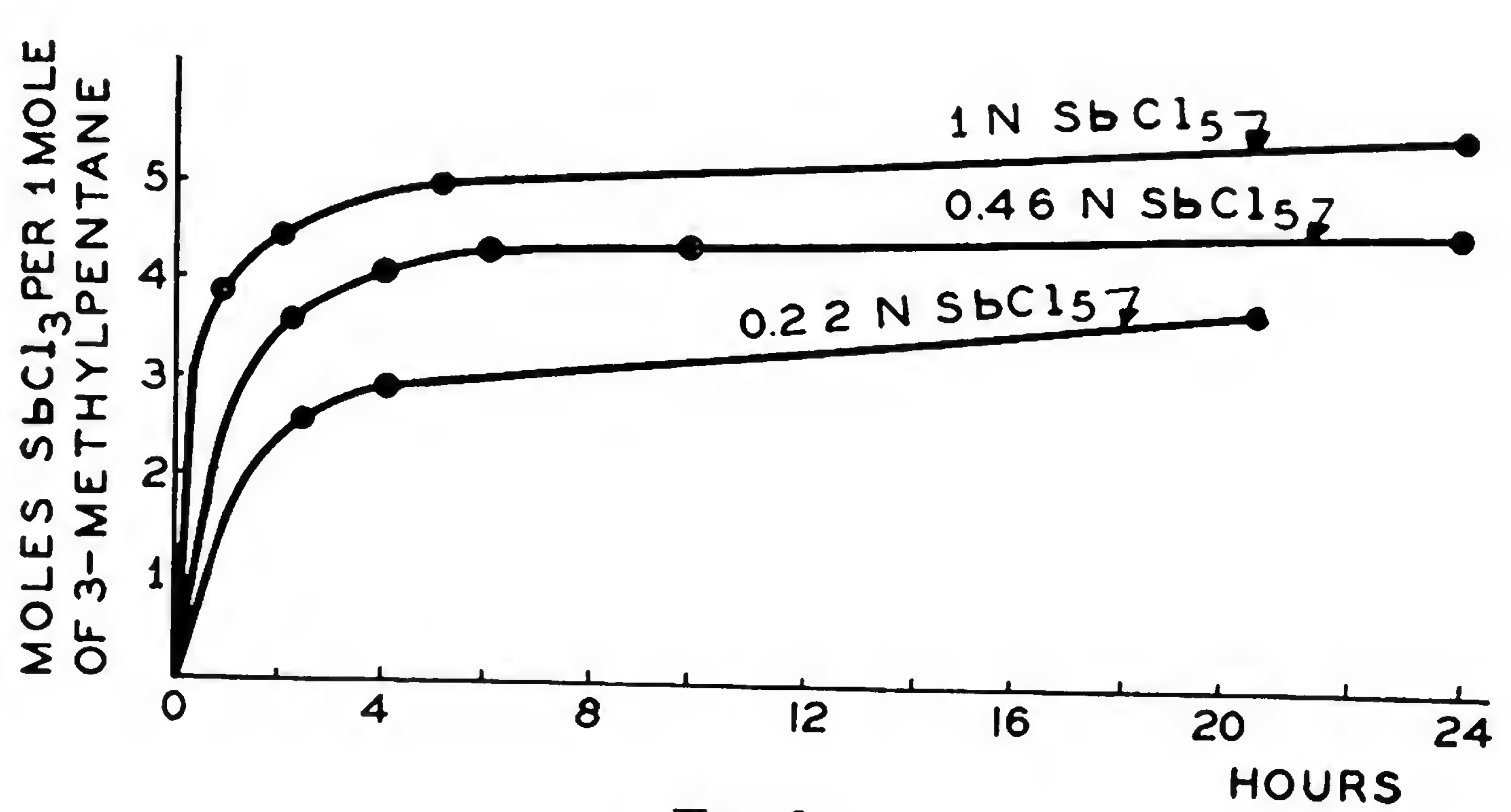


FIG. 2.

Chlorination of hexanes in the presence of P_2O_5: The absence of precipitation in the reactions using P_2O_5 allowed us to simplify the procedure, since several tests could be conducted from a given vessel. The method will be described at the end of this article. Figure 2 shows the influence of concentration of the $SbCl_5$ solution on the degree of chlorination for 3-methylpentane in the presence of P_2O_5. All the experi-

ments were carried out with a 12:1 mole relationship of $SbCl_5$ to hydrocarbon. By comparison with the data presented in Figure 1, it can be seen that $SbCl_5$ solution dried over P_2O_5 reacts much more energetically. However, the same relationship exists between concentration of $SbCl_5$ and the degree of chlorination as in the work without P_2O_5.

Experiments wherein the concentration of both components (iso-compounds and $SbCl_5$) was varied are considered in Table 2.

Table 2.

Conc. of $SbCl_5$ Solution	Content of 2-Methylpentane in the Reaction Mixture (%)	Moles of $SbCl_5$ for 1 Mole of Iso-compound	Number of Moles of $SbCl_3$ Formed per 1 Mole of 2-Methylpentane during 1 hour	2 hours	4 hours	6 hours
0.69 *N*	0.24	24	4.4	4.9	5.5	..
0.69 *N*	0.12	48	4.6	5.2	5.8	..
0.69 *N*	0.06	96	3.7	5.2	6.0	..
0.34 *N*	0.24	12	3.1	4.0	4.7	..
0.34 *N*	0.12	24	3.4	4.3	5.0	..
0.34 *N*	0.06	48	2.4	4.4	5.7	..
0.17 *N*	0.24	6	1.0	2.0	2.7	3.2
0.17 *N*	0.12	12	0.3	1.6	2.5	3.6
0.17 *N*	0.06	24	0.2	0.4	1.5	3.3

The experiments were carried out with solutions of 2-methylpentane and $SbCl_5$ in $CHCl_3$ in the presence of P_2O_5.

The role of iso-hexane structure upon the degree of chlorination is shown in Figure 3. Experiments with 12:1 mole relationship of $SbCl_5$ to iso-compound were carried out with 0.22*N* solution of $SbCl_5$ in $CHCl_3$

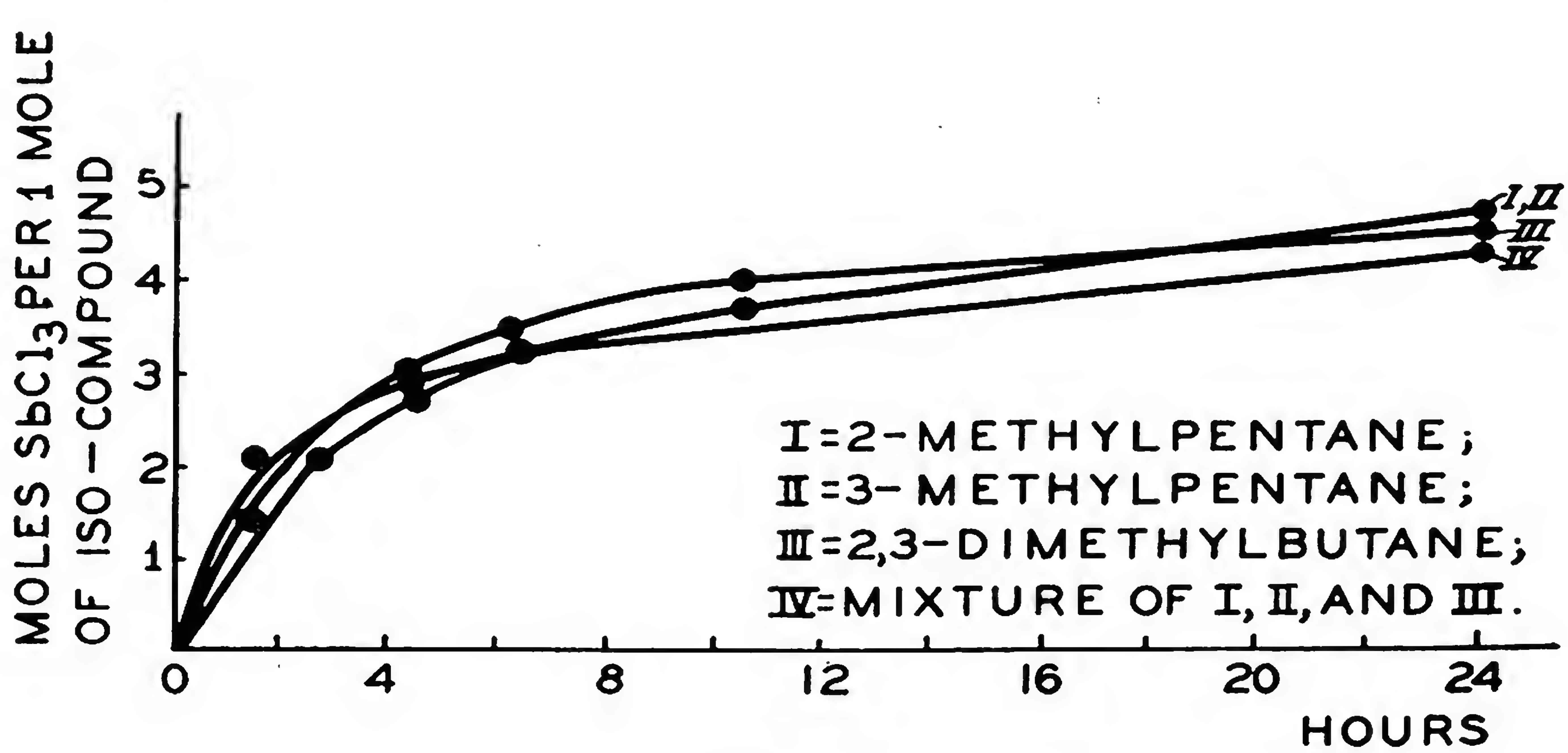


FIG. 3.

in the presence of P_2O_5. The results were very close, particularly after several hours. Slight differences in the degree of chlorination for the different isomers are due to experimental error, when one takes into consideration that only 15-30 mg. of iso-compound were taken for an experiment. An investigation of the action of $SbCl_5$ on *n*-hexane in the

presence of P_2O_5 showed that this hydrocarbon is slightly chlorinated, particularly with solutions stronger than $0.5N$ (this depends on the purity of the material used).* However, in the chlorination of hexane and iso-compound mixtures with $SbCl_5$ solutions not exceeding $0.46N$, the degree of chlorination does not exceed the combined amounts of chlorination in the components, as shown in Table 3. It is necessary to remark that,

Table 3.

	Number of Moles of $SbCl_3$ Formed per 1 Mole of Hydrocarbon							
	0.22N Solution of $SbCl_5$					0.46N Solution of $SbCl_5$		
Time (hrs.)	n-Hexane	2-Methyl-pentane	n-Hexane + 6% of 2-Methyl-pentane	2,3-Di-methyl-butane	n-Hexane + 6% of 2,3-Di-methyl-butane	n-Hexane	3-Methyl-pentane	n-Hexane + 8% of 3-Methyl-pentane
2	0.1	2.1	2.3	2.4	2.4	..	3.4	3.5
4	0.15	2.9	3.1	3.0	3.0	0.1	3.8	4.0
6	0.2	3.3	3.5	3.2	3.3	0.2	4.2	4.5
10	0.4	3.7	4.0	3.6	3.7	0.3	4.4	5.0
24	0.5	4.5	5.2	4.3	4.7	0.75	5.1	5.9

in order to have comparable results, the number of $SbCl_5$ molecules taken for hexane chlorination was calculated for the amount of iso-compound contained in the solution. Actually, the consumption of $SbCl_5$ and hexane consists of only a part of the total.

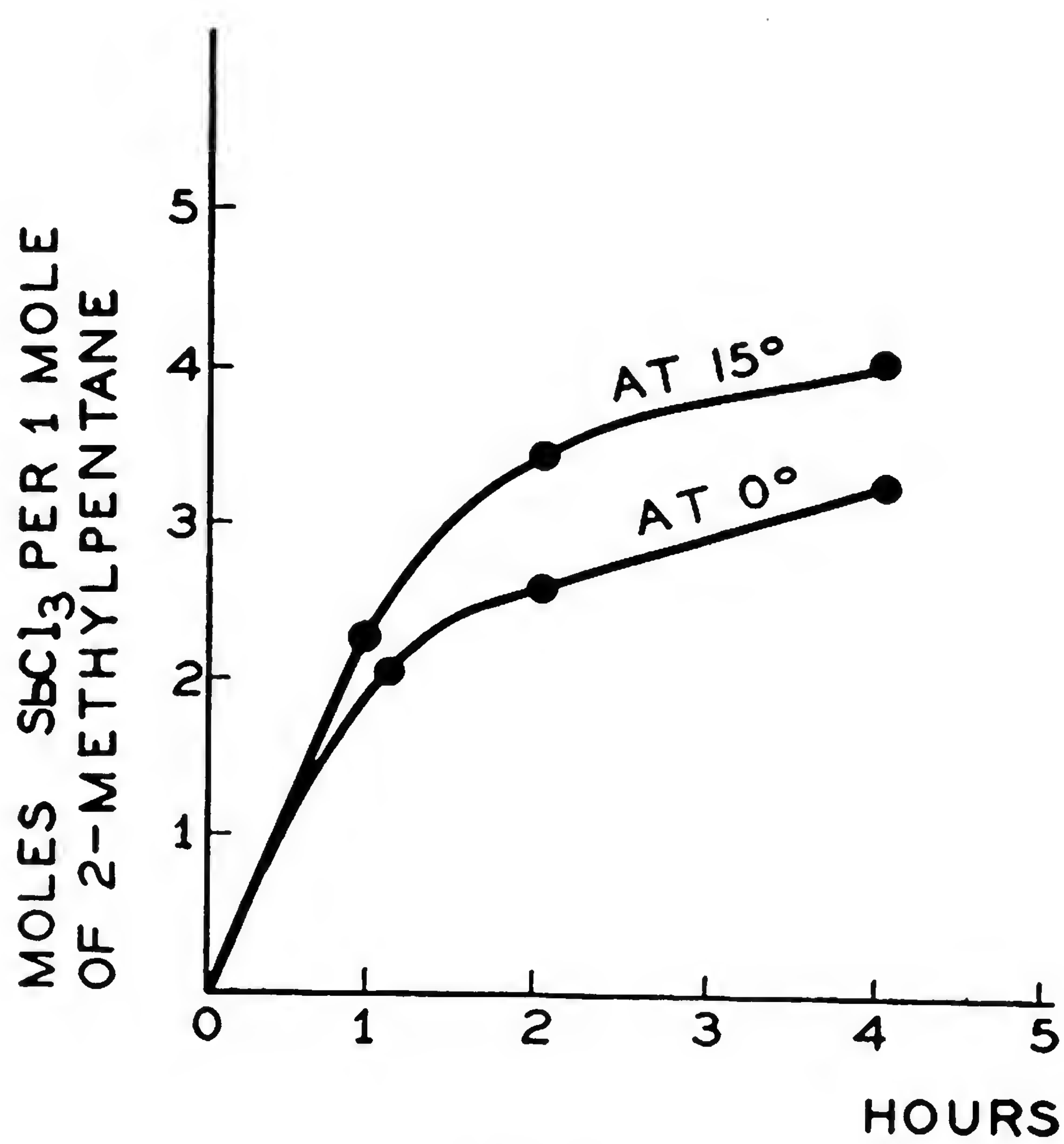


FIG. 4.

* As indicated by Schaarschmidt [*Z. angew. Chem.*, 46, 153 (1933)], the normal hydrocarbons obtained from the hydrocarbon mixtures treated with $SbCl_5$ are less stable to this reagent than the synthetic hydrocarbons. By this we probably can explain the lower stability toward $SbCl_5$ of our synthetic hydrocarbons purified by $SbCl_5$.

Figure 4 shows the influence of temperature on the speed of iso-hexane chlorination. The experiments were carried out at two temperatures with 2-methylpentane and $0.3N$ solution of $SbCl_5$ in 1:18 molar ratio.

The Action of $SbCl_5$ on Octane and Its Isomers

The action of $SbCl_5$ was studied on n-octane and two isomers: 4-methylheptane with one tertiary carbon atom and 2,5-dimethylhexane with two tertiary carbon atoms. The experiments on chlorination of 2,5-dimethylhexane and 4-methylheptane showed that these hydrocarbons are chlorinated more slowly than iso-hexanes, as evident from Table 4.

Table 4.

Hydrocarbon Taken, in % of $SbCl_5$ Solution			Moles of $SbCl_5$ to 1 Mole of Iso-compound	Number of Moles of $SbCl_3$ Formed per 1 Mole of Iso-compound during	
2,5-Dimethyl-hexane	4-Methyl-heptane	2-Methyl-pentane		2 hours	4 hours
0.11	...	...	48	2.5	4.1
...	0.11	...	48	2.9	3.9
...	...	0.10	40	4.7	5.1
0.34	...	...	15	2.5	4.0
...	0.34	...	15	2.5	3.5

The experiments were carried out with $0.5N$ $SbCl_5$ at room temperature in the presence of P_2O_5. As in the case of 2,3-dimethylbutane, the second tertiary carbon atom of 2,5-dimethylhexane had no effect on the speed of chlorination.

Experiments carried out to see if n-octane is chlorinated when present alone or with its isomers have showed that pure n-octane is not chlorinated under the given conditions. No induced chlorination was observed after addition of iso-octanes (using $0.72N$ $SbCl_5$) (Table 5).

Table 5.

Time hrs.	Number of Moles of $SbCl_3$ Formed per 1 Mole of Iso-octane: $0.5N$ $SbCl_5$ — 4-Methyl-heptane	$0.5N$ $SbCl_5$ — n-Octane with 5% of 4-Methylheptane	$0.72N$ $SbCl_5$ — 2,5-Dimethyl-hexane	$0.72N$ $SbCl_5$ — n-Octane with 7% of 2,5-Dimethylhexane
2	2.9	3.0	4.6	4.6
4	3.8	3.9	5.6	6.0
6	4.2	4.4	..	..

The question remains open whether this can be explained by a greater purity of our synthetic octane as compared to hexane or by a greater stability. The experiments were conducted with a 46:1 molar ratio of $SbCl_5$ to iso-octane. Under the assumption that the other isomeric octanes will behave the same, the results indicate that the method of analysis using $SbCl_5$ can be used for mixtures of iso-octanes.

Mechanism of chlorination by means of $SbCl_5$: From the foregoing statements, it is evident that from 4 to 5 or more moles of $SbCl_5$ are consumed for 1 mole of iso-compound, depending on the concentration of the reactants. It was impossible to stop the reaction at the first stage of

chlorination when using excess of $SbCl_5$. The mechanism of the reactions occurring seems to us to be the following: first, the $SbCl_5$ reacts with hydrogen of the tertiary carbon atom. The resulting tertiary chloride in the presence of $SbCl_5$ splits off hydrogen chloride, and chlorine adds to the new double bond with the formation of dichloride. From the latter, hydrogen chloride is split off, chlorine is again added to the double bond, and so on. An analogous mechanism was proposed by A. Kronstein [323a] to explain bromination of halogen derivatives in the presence of iron. Directive action of iron for bromination at atoms adjacent to those containing halogen was explained by the fact that the iron forms ferric bromide on its surface at the beginning of the reaction, and the scission giving hydrogen bromide is thus catalyzed. An analogous or similar catalytic action must be ascribed to $SbCl_5$ during chlorination. This substance acts like other metal halides, for instance, in the Friedel-Crafts and other reactions.

A certain energy of activation is necessary for the introduction of the first atom of chlorine, since the chlorination of hydrocarbons is an exothermic reaction. This energy of activation is probably greater than that for the succeeding steps, since chlorination, when once started, does not stop. The reaction is analogous to the oxidation of methane, which is difficult to stop at the intermediary oxidation stage giving formaldehyde. The active molecules of chloride can activate the normal hydrocarbons contained in the mixture and induce the reaction between them and the $SbCl_5$. We probably can explain by this fact the induced chlorination of normal hydrocarbons. Stewart and Hanson,[565a] for instance, observed the same phenomenon during the chlorination of ethylene in the dark in the presence of benzene. The induced reaction, $3Cl_2+C_6H_6 \rightarrow C_6H_6Cl_6$ occurred, though not by itself in the dark. The authors explained this phenomenon by applying the chain mechanism. It is necessary to note the following also. In our experiments, the degree of chlorination of iso-compounds was calculated from the total expenditure or use of $SbCl_5$. Whether or not a part of the iso-structure hydrocarbon remains unattacked, or whether all the molecules are equally chlorinated, and the dependence of these upon the process conditions, are still unsolved. Several experiments on chlorination of chlorides were carried out in

Table 6.

Halogen Derivative	Experiment Time (hrs.)	Moles of $SbCl_3$ Formed per 1 Mole of Chloride
Propyl Chloride	2	0
2-Chloro-2-methylbutane	0.5	0.96
2-Chloro-2-methylbutane	2	1.05
2-Chloro-2-methylbutane + Propyl Chloride (1:1)	2	0.95[a]
2-Chloro-2-methylpropane	2	0.98

[a] Calculated on tertiary chloride.

order to prove our ideas on the mechanism of chlorination. These experiments were conducted under the conditions mentioned in the beginning of this article, *i.e.*, $0.1N$ $SbCl_5$ in CCl_4 at 0°, and are presented in Table 6.

From the table, it is evident that tertiary chlorides react even with a $0.1N$ solution of $SbCl_5$ in CCl_4. The reaction ends at the disubstituted stage, but the chlorination of iso-structure hydrocarbons, as already shown, requires $2\text{-}2.5N$ solution of $SbCl_5$ in CCl4 (without P_2O_5). As expected, the action of a $2N$ solution of $SbCl_5$ in chloroform on the tertiary chlorides does not stop at monochlorination but continues to 3 or 4 molecules, as in the case of hydrocarbons. The experiments demonstrate the greater ease of the second stage of chlorination that is connected with HCl evolution and the addition of chlorine at the double bond. We did not continue the study of the action of $SbCl_5$ on chloro-derivatives; however, a detailed study would be of great value for the development of an analytical method for tertiary chlorides.

Summarizing the foregoing statements, it is an obvious conclusion that the complex action of $SbCl_5$ on hydrocarbons does not permit us to apply a definite kinetic equation to the process. However, sufficient data have been obtained to develop a practical method for the analysis of mixtures of isomeric hexanes or octanes. An independence of chlorination speed and iso-compound structure (for iso-hexanes and iso-octanes among themselves) allows us to compare the degree of chlorination in unknown mixtures with that of a control hydrocarbon. A description of a practical method follows.

Method of Analysis of *n*-Hexane and Octane in Mixtures Containing their Isomers

A $0.5N$ solution of antimony pentachloride in chloroform is first prepared. The chloroform for this purpose is washed by sulfuric acid, sodium carbonate, and water, dried, and distilled. It is then dried by P_2O_5.* The purified chloroform is introduced into a ground, glass-stoppered flask, and the required amount of $0.4\text{-}0.6N$ solution of $SbCl_5$ is added. Next, P_2O_5 is inserted. The solution is shaken for 0.5 to one hour, after which it is allowed to settle until all the P_2O_5 has deposited as a compact layer at the bottom, with a clear solution of $SbCl_5$ above. From two to three ml. of this solution are titrated to determine the amount of $SbCl_5$ and $SbCl_3$. If necessary, the solution is concentrated by $SbCl_5$ addition or diluted with the foregoing chloroform. The determination of iso-compounds is conducted as follows: 0.25 ml. of some iso-compound in octane or hexane containing a definite concentration (5-10%) is added to a graduated cylinder (I) of 25 ml. capacity; 0.5

* This purification is recommended, otherwise the $SbCl_5$ solution changes its factor.

ml. of the solution to be investigated is introduced into a cylinder (II) of the same capacity. If the specific gravity is unknown, one can measure the investigated materials by weight in sealed glass ampoules instead of micropipetting. Both cylinders are filled to the mark (15-25 ml., depending on the expected amount of isomers) with $SbCl_5$ solution, and a small quantity of P_2O_5 is added to each. The cylinders are shaken and then left alone. After several minutes the reaction starts; this may be noticed by the color change. The solution, which was originally light yellow, becomes gradually red and then dark brown. Sometimes, the reaction does not start immediately, but the solution is usually dark at the end of the first hour. After 2-3 and 4-6 hours, 3 ml. of solution are pipetted from each cylinder and titrated for $SbCl_3$ content by means of $0.1N$ $KBrO_3$ solution, as previously indicated. The pipette must be protected by a calcium chloride tube to avoid introduction of moisture into the cylinder during withdrawal of the sample. Since only a few ml. of solution are necessary for the titration, we used a 10 ml. burette with 1/20 ml. divisions. A parallel determination of $SbCl_3$ is made on a 3 ml. sample of the original solution of $SbCl_5$ in chloroform, and the amount thereof is used as a correction for the titrations.

It is possible to calculate the weight per cent of iso-compound within the unknown sample by comparing the titration results for the cylinder II sample with those for cylinder I during the same time of chlorination, according to the following formula,

$$x = \frac{a \cdot c \cdot e \cdot f}{b \cdot d \cdot g}$$

where a is the number of ml. of $0.1N$ $KBrO_3$ that was used for the titration of 3 ml. from cylinder II; b is the number of ml. of $0.1N$ $KBrO_3$ solution that was used for the titration of 3 ml. of solution from control cylinder I; c is the number of ml. of $SbCl_5$ solution placed in cylinder II; d is the number of ml. of $SbCl_5$ solution placed in cylinder I; e is the weight per cent of iso-compound in the hexane- or octane control solution for cylinder I; f is the number of ml. of the control solution; and g is the number of ml. of the unknown solution being analyzed. The results obtained for 2-3 and 4-6 hours usually differ very little. However, in certain cases where the beginning of the reaction proceeds slowly (at low concentration of iso-compound), the results are more accurate after 4-6 hours, since the difference in velocity of chlorination is thereby compensated. Tests of longer duration are not advisable, because the chlorination velocity becomes very slow. It is possible for the initial molar ratio of $SbCl_5$ to iso-compound to be less than 12:1 whenever the content of iso-compounds is large. The amount of unused $SbCl_5$ must be calculated after the analysis,

since it is not recommended to work below this limit. If less than 6-7:1 molar ratio prevailed, the analysis must be repeated and the amount of hexane or octane decreased to 0.2-0.3 ml.

Finally, we present in Table 7 the results of analyses for several control mixtures containing isomers within *n*-hexane and octane. These

Table 7.

Expt. No.	Mixture Taken for the Analysis		Control Solution	Indicated Percentage of Iso-compound 2 hrs.	3 hrs.	4 hrs.	6 hrs.
1	5% 2,5-Dimethylhexane 5% 4-Methylheptane	in 0.5 ml. of *n*-Octane	5% 4-Methylheptane in 0.5 ml. of *n*-octane	11.6	...	11.9	...
2	12.5% 2,5-Dimethylhexane 12.5% 4-Methylheptane	in 0.5 ml. of *n*-Octane	5% 4-Methylheptane in 0.5 ml. of *n*-octane	28.3	...	28.0	...
3	10% 2,5-Dimethylhexane 10.8% 4-Methylheptane	in 0.6 ml. of *n*-Octane	5% 2,5-Dimethylhexane in 0.6 ml. of *n*-Octane	...	18.6	...	21.4
4	4.8% 2,3-Dimethylbutane 4.5% 2-Methylpentane	in 0.5 ml. of *n*-Hexane	5.5% 2-Methylpentane in 0.5 ml. of Hexane	...	9.0	...	8.8
5	10% 2,3-Dimethylbutane 10.5% 2-Methylpentane	in 0.5 ml. of *n*-Hexane	5.5% 2-Methylpentane in 0.5 ml. of Hexane	...	19.7	...	19.5
6	4.5% 2,3-Dimethylbutane 4.5% 4-Methylheptane	in 0.6 ml. of *n*-Octane	Control Solution #4	...	9.5	...	9.2
			Control Solution #1	...	7.8	...	8.0

analyses were conducted according to the method described. From this table, it can be seen that the results were very close, particularly if the small amount of iso-compound used in the analysis is taken into consideration. A mixture of an iso-hexane and an iso-octane was used in experiment 6. The results of its analysis were calculated by using iso-octane and also iso-hexane (as the basis of control), as can be seen from Table 7. Even in such cases, the results were satisfactory. We suggest the future extension of this method's utility to the study of different mixtures of hydrocarbons containing a tertiary carbon atom, because this problem has exceptional importance in the study of motor fuels. We can mention that preliminary chlorination experiments on cyclohexane in its mixture containing methylcyclohexane showed a complete possibility of quantitative determination.

Conclusions

1. Chlorination of isomeric hexanes and octanes was studied quantitatively by determination of $SbCl_5$ expenditure.

2. Compounds containing hydrogen on a tertiary carbon atom are readily chlorinated by dilute $SbCl_5$ solutions.

0.2–0.3N

the analysis.

origins.

Appendix II

The following translation of O. W. Bauer's Thesis, Eidgenössischen Technischen Hochschule, Zürich, pp. 54-60 (1940), covers some fundamental work on iso-alkane determination. It is submitted for the perusal of readers interested in the quantitative estimation of alkane isomers by means of physical methods based on "additive functions."

Determination of the Number of Side-Chains in Alkanes by Means of the Parachor

Marder in an extensive article [358a] discusses the application of physical constants to the study of motor fuel composition. In the following article we will discuss the use of the parachor in analysis of hydrocarbons.

Sugden [574c] suggested an expression, called parachor, which is a constant, independent of temperature, for every pure chemical compound:

$$P = s^{1/4} \cdot \frac{M}{D}$$

P = Molecular parachor
s = Surface tension at the temperature $t°$
M = Molecular weight
D = Density of the compound in the liquid phase at the temperature $t°$

The advantage of the parachor is its additive property which, as with molecular refraction, permits it to be calculated from atomic contributions. These atomic contributions are called increments and are determined empirically. Values calculated from them check well with those determined by the above formula.

As can be seen, the molecular parachor strongly depends on molecular weight. Since hydrocarbon mixtures nearly always contain compounds with different molecular weights, it is advantageous to use the specific parachor, which is the parachor value for 1 gram of substance:

$$p = \frac{1}{D - \frac{M}{24055}} \cdot s^{1/4}$$

The molecular parachors and specific parachors decrease in the following sequence: alkanes, alkenes, naphthenes, and aromatics. The analytical method of Marder for determination of these hydrocarbon classes is based on this property. Since the present work concerns only alkanes, we shall continue with a discussion of the differences in alkane parachors.

When the parachors of alkanes are calculated from the increments, there is no difference between normal and iso-alkane values. However, when the parachor is determined from the physical constants for various isomers of a certain alkane, there is a remarkable deviation from the theoretical value. This deviation increases with the number of side-chains. Both parachors, P and p, decrease with increasing branching. The decrease in molecular parachor averages about 2.5 per side-chain. This requires that the increments assume different values for secondary, tertiary, and quaternary carbon atoms.

From the parachor measurement for an alkane mixture, it is possible to determine the average degree of branching of the alkanes, provided no other classes of hydrocarbons are present. The molecular parachor increases with increase in molecular weight and decreases with increase in branching. The specific parachor, on the contrary, decreases with increase in molecular weight and with increase in branching.

A determination can be conducted in the following manner: First, curves of parachors *versus* molecular weight are constructed for normal, monosubstituted, disubstituted, and higher-substituted alkanes. Then the unknown mixture of alkanes is carefully separated into fractions of the same molecular weight, and physical measurements are made on these fractions. The degree of branching in the unknown mixture is obtained by a comparison of the results of these measurements with the curves. The original literature must be consulted for a detailed discussion of the theory of the parachor.[358a, 574c]

Procedure of Measurement

The density and surface tension of the investigated alkanes must be measured in order to determine the specific parachor. The density is measured by means of a picnometer with ground glass cap and thermometer and of 10 cc. capacity. For the surface tension measurement, Marder suggests the capillary rise apparatus of Ubbelohde[600b] as a very accurate one. However, the maximum bubble pressure method of Sugden[574a, 574b] was tried first.

The principle of this method consists of the following: two glass tubes of different diameters are placed in the liquid to be investigated and air is drawn through them. The pressure difference upon suction through the two tubes is a measure of the surface tension. The original literature[574a, 574b] must be consulted on account of the somewhat complicated theoretical basis of this method. The surface tension is calculated by means of the following formula:

$$s = A \cdot P\left(1 + 0.69\, r_2 \cdot \frac{gD}{P}\right)$$

s = Surface tension at the temperature $t°$
A = Previously determined constant for the apparatus
P = Observed pressure difference (height × density of the liquid × acceleration of gravity)
r_2 = Radius of the wider tube
g = Acceleration of gravity
D = Density of the liquid at the temperature $t°$

In order that the calculation may require the diameter of only the wider tube, the other tube is selected as narrow as possible, that is to say, a capillary is used. The diameter, r_2, of the wider tube is measured very carefully with the aid of a magnifying glass. The pressure, P, is measured by means of a U-tube containing an indicating liquid. It is immaterial what kind of manometer fluid is used, provided that its density is known. Distilled water, colored red by a drop of acid and methyl orange, was used. Its density was taken as that of distilled water. The suction required to pull air through the tubes was obtained by attaching a dropping funnel filled with mercury to the apparatus. The velocity of air suction was controlled by regulating the speed of mercury withdrawal. The entire arrangement consists, therefore, of a measuring apparatus with two tubes, the dropping funnel with mercury, and the manometer (U-tube). The required quantity of hydrocarbon liquid was 1.5 to 2 cc. [For a description of the apparatus, etc., see S. Sugden, *J. Chem. Soc.* **121,** 858-866 (1922); **125,** 27-31, 1177-1189 (1924)].

Before proceeding with an actual measurement, the apparatus constant, A, must be determined. Benzene was used for this purpose because its surface tension and density are well known. The benzene must be chemically pure, which means thiophene-free but not absolutely free of water, since traces of moisture do not affect the surface tension of benzene. One could determine the apparatus constant also with pure distilled water. However, this is not advisable, since the surface tension of water differs too much from that of hydrocarbons.

During the measurement, the apparatus must be kept at constant temperature. Since most of the measurements were conducted at room temperatures, it was sufficient to use a beaker with water or paraffin oil, as the thermostat.

The disadvantage of Sugden's method consists of a partial evaporation of the liquid and its gradual change in composition caused by the passage of air. However, taking into consideration that the differences in the vapor pressure of isomers are very small and that the experiment is carried out in a very short time, the changes in composition cannot be excessive.

The other method of determining the surface tension is the capillary rise method of Ubbelohde.[600b] Here, also, the extensive theoretical basis cannot be given, and the original literature must be consulted.

The arrangement is somewhat simpler than Sugden's. The apparatus consists of two tubes and a capillary, which are sealed parallel to each other onto a small vessel. The capillary is calibrated and represents the most important part of the apparatus. The following procedure is used: The liquid is introduced into the widest tube up to the mark and the whole apparatus placed in a thermostat consisting of a beaker filled with water or paraffin oil. After the liquid attains the temperature of the thermostat, it is forced high into the capillary by means of a rubber bulb, so that a little liquid flows out. The pressure is then released, whereupon the liquid will settle in the capillary at different heights, depending on its surface tension. The height is measured, as in Sugden's method, by means of a cathetometer within an accuracy of ± 0.05 mm.

This apparatus also must be standardized. A calibration of the capillary is required. The standardization is again carried out with benzene. The surface tension is calculated by means of the following formula:

$$s = h \cdot D \cdot \frac{s_B}{h_B \cdot D_B}$$

s = The observed surface tension at the temperature $t°$
h = Capillary rise of the observed liquid at the temperature $t°$
D = Density of the observed liquid at the temperature $t°$
s_B = Surface tension of benzene at the temperature $t_1°$
h_B = Capillary rise of benzene at the temperature $t_1°$
D_B = Density of benzene at the temperature $t_1°$

For the ensuing work, we used a standardized apparatus that was kindly loaned by the "Institute for Brown Coal and Mineral Oil Research" of the Berlin Technischen Hochschule. The calculation followed the formula:

$$s = h \cdot D \cdot k, \quad \text{whereby} \quad k = \frac{s_B}{h_B \cdot D_B}$$

It was necessary to add 0.280 to the observed height for the uncalibrated part.

The following tables represent the results of a standardization of Sugden's apparatus and of measurements on n-octane, 2-methylheptane, and their mixtures.

Table 1. Determination of the Apparatus Constant A.

$$A = \frac{s}{P\left(1 + 0.69\, r_2 \cdot \frac{gD}{P}\right)}$$

Expt. No.	Height (cm.)	Temp. (°C.)	Density of Benzene, $D_4{}^t$	Surface Tension of Benzene s_t	Apparatus Constant, A
83	9.19	16.0	0.8830	29.40	0.003115
84	0.03	20.0	0.8791	28.85	0.003114
85	8.93	22.0	0.8769	28.59	0.003115
86	8.89	23.0	0.8760	28.46	0.003114
87	8.80	25.0	0.8738	28.23	0.003123
88	8.75	26.0	0.8727	28.10	0.003119
89	8.67	28.0	0.8704	27.84	0.003118
				Average	0.003117

The average value was 0.003117. It was used in the following measurements of parachor.

Table 2. Determination of the Parachors of Various Octanes.
Determination of the Surface Tension and Parachor of n-Octane

Expt. No.	Temp. (°C.)	Density $D_4{}^t$	Height (cm.)	Surface Tension	Molecular Parachor, P	Specific Parachor, p
90	22.0	0.7007	6.805	20.75	349.9	3.066
91	24.0	0.6991	6.705	20.54	349.8	3.065
92	25.0	0.6983	6.69	20.49	350.0	3.067
93	28.0	0.6958	6.61	20.10	349.5	3.063
				Average	349.8	3.065

Averaging of the parachor measurements for n-octane gave:

Molecular parachor	349.8
Specific parachor	3.065

Determination of the Surface Tension and Parachor of 2-Methylheptane

Expt. No.	Temp. (°C.)	Density $D_4{}^t$	Height (cm.)	Surface Tension	Molecular Parachor, P	Specific Parachor, p
94	14.6	0.7038	6.72	20.58	347.7	3.047
95	21.4	0.6982	6.52	19.98	347.7	3.047
96	22.6	0.6973	6.475	19.86	347.7	3.047
97	24.8	0.6955	6.405	19.63	347.7	3.047
98	30.0	0.6913	6.245	1910	347.3	3.043
				Average	347.7	3.047

Averaging of the parachor measurements for 2-methylheptane gave:

Molecular parachor	347.7
Specific parachor	3.047

Determination of the Surface Tension and Parachor of 2,2,4-Trimethylpentane

Expt. No.	Temp. (°C.)	Density $D_4{}^t$	Height (cm.)	Surface Tension	Molecular Parachor, P	Specific Parachor, p
99	10.8	0.6983	6.205	19.05	343.9	3.013
100	17.0	0.6934	6.04	18.53	343.9	3.013
101	22.0	0.6895	5.90	18.09	343.8	3.011
102	24.6	0.6875	5.82	17.80	343.4	3.009
				Average	343.7	3.012

Averaging of the parachor measurements for 2,2,4-trimethylpentane gave:

Molecular parachor	343.7
Specific parachor	3.012

[illegible]
50% 2-Methylheptane

Specific Parachor, P_s	Molecular Parachor, P
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
3.05[illegible] Average	348.7

[illegible] 50 per cent 2-methyl[illegible]

Molecular parachor [illegible]
Specific parachor [illegible]

[illegible]

Appendix III

Since the main part of this monograph was written, new material has appeared which was thought highly desirable for incorporation as a supplement in the interest of bringing the data up to February 1, 1942.

The importance of the isomerization of normal butane, pentane, hexane, and naphtha in the production of 100 octane gasoline, which makes possible the tremendous speeds and load-carrying capacities of today's airplanes, is indeed great. Furthermore, the isomerization of normal butane into isobutane, followed by dehydrogenation to isobutene, supplies a base material for polymerization in "butyl rubber" production.

In the United States, South America, and the Near East, isomerization plants are under commercial construction or operation [Anon., *Refiner Natural Gasoline Mfr.*, **21,** 103 (1942)]. These plants produce isobutane from *n*-butane for the synthesis of 2,2,4-trimethylpentane or can isomerize "ordinary gasoline" into aviation gasoline or its components. They are obviously opening new fields for the use of natural, casinghead, and straight-run gasolines, which are readily isomerizable into branched-chain hydrocarbons of more appropriate octane rating and combustion properties. These trends call for latest data on both pure and applied isomerizations.

Pure Isomerization

Heats of combustion of simple aliphatic and cyclic hydrocarbons at constant pressure have been investigated by V. P. Golmov [*J. Gen. Chem. (U.S.S.R.),* **11,** 405-410 (1941)].* Hydrogen atoms attached to primary, secondary, and tertiary carbon atoms were given increasing thermochemical values of 30.7, 31.4, and 31.7 kilocalories per gram-atomic weight, respectively. The excess of energy in cyclic hydrocarbons as compared with their aliphatic isomers was also considered. Since this article is concerned with the calculation of theoretical values of heats of combustion, its scope can be readily extended to yield theoretical values of heats of isomerization.

Heat capacity data for gaseous 2,2,4-trimethylpentane at 150-185° and zero or atmospheric constant pressure have been published by M. Kiperash and G. S. Parks [*J. Am. Chem. Soc.,* **64,** 179 (1942)]. The consistency of the observed data and corresponding values calculated

* A complete translation by J. G. Tolpin appears in Universal Oil Products Company Survey of Foreign Petroleum Literature, September 5, 1941.

from the statistical equation of K. S. Pitzer [*J. Am. Chem. Soc.*, **62,** 1224-1227 (1940)], is considered as reasonable, the deviations being around 1.5 per cent. The foregoing data are part of a soundly based "thermodynamics of isomerization."

Heats of formation and of combustion for the 9 isomeric heptanes in the liquid state at 25° and atmospheric pressure have been reported by G. F. Davies and E. C. Gilbert [*J. Am. Chem. Soc.*, **63,** 2730-2732 (1941)]. The exothermic heats of isomerization of *n*-heptane into 2-methylhexane, 3-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane for these conditions of state were obtained directly from the heats of combustion and reported as 1.25, 0.52, 0.19, 3.91, 1.70, 2.985, 3.025, and 2.80 kilocalories per gram-mole, respectively. Heats of isomerization of *n*-heptane into its 8 isomers have been determined also by E. J. R. Prosen and F. D. Rossini [*J. Research Natl. Bur. Standards*, **27,** 519-528 (1941) (Research Paper No. 1439)]. Their values for the liquid state at 25° and atmospheric pressure are in substantial accordance with those of Davies and Gilbert, being 1.30 ± 0.25, 0.72 ± 0.25, 0.14 ± 0.23, 3.42 ± 0.28, 2.18 ± 0.26, 2.54 ± 0.16, 2.44 ± 0.15, and 3.00 ± 0.22 kilocalories per gram-mole for the given order of branched heptanes. The corresponding values for the ideal gaseous state at 25° C. were reported by Prosen and Rossini as 1.80 ± 0.29, 1.18 ± 0.29, 0.52 ± 0.27, 4.45 ± 0.32, 2.80 ± 0.30, 3.40 ± 0.22, 3.24 ± 0.21, and 4.17 ± 0.27 kilocalories per gram-mole, respectively. For the exothermic heats of isomerization of *n*-octane into 2-methylheptane and 3-methylheptane in the liquid state at 25° and atmospheric pressure, the latter investigators cite unpublished values of 1.50 ± 0.30 and 0.63 ± 0.30 kilocalories per gram-mole, respectively.

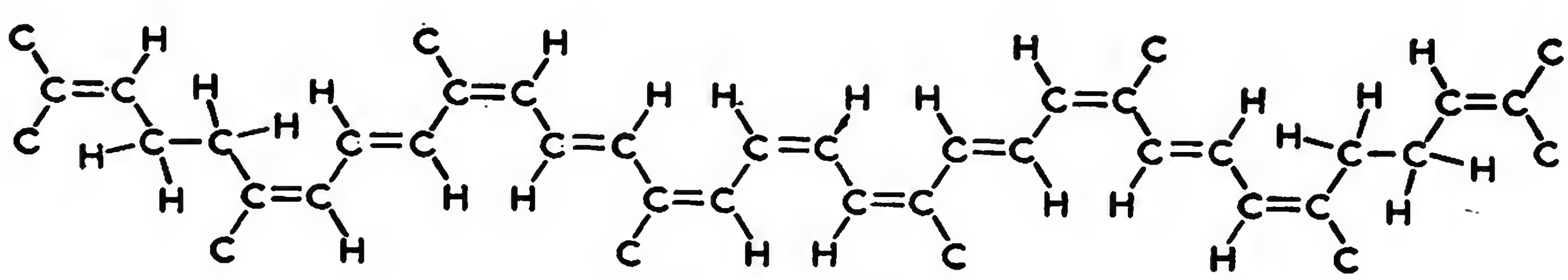
The isomerization of *n*-butane at 120° in the presence of one-fifth its weight of aluminum chloride and some water yielded upwards of 50 per cent of isobutane for a contact time of 30 minutes, according to O. Ferrari [*Rev. facultad cienc. quim. (Univ. nacl. La Plata)*, **15,** 297-305 (1940); *Chem. Abs.*, **35,** 7365 (1941)].

A short review on "Isomerization of Unsaturated Hydrocarbons," including several related reactions of hydrocarbons, alcohols, and carboxylic acids, has been published by E. Bergmann [*Chem. Rev.*, **29,** 529-551 (1941)].

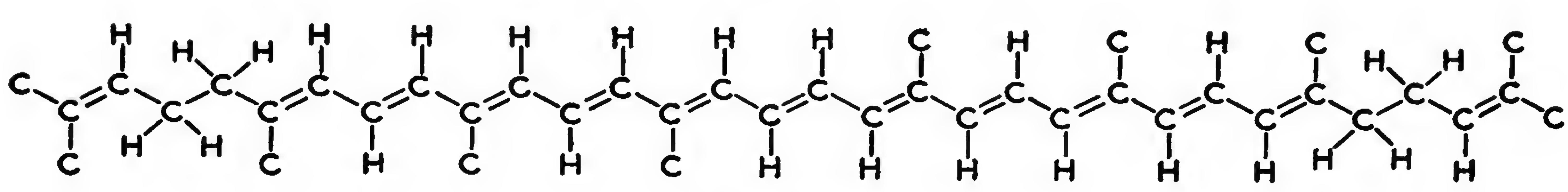
The work of R. H. Ewell and P. E. Hardy on "Isomerization Equilibrium among the Branched Chain Pentenes," which was presented as a Petroleum Division Paper at the Atlantic City Meeting of the American Chemical Society, has been revised and published [*J. Am. Chem. Soc.*, **63,** 3460-3465 (1941)]. It should be read by those interested in isomerization of either straight or branched-chain pentenes, in provisional values

of the absolute entropies of the latter pentenes, or in their entropies of isomerization.

6,7-10,11-14,15-16,17-18,19-22,23-26,27-*cis*-8,9-12,13-20,21-24,25-*trans*-2,6,10,14,19,23,27,31-Octamethyldotriacontatridecaene-2,6,8,10,12,14,16,-18,20,22,24,26,30 is the structure assigned to prolycopene, the principal pigment of ripe tangerine tomato fruits, by L. Zechmeister, A. L. LeRosen, F. W. Went, and L. Pauling [*Proc. Nat. Acad. Sci. U. S.*, **27**, 468-474 (1941)]. These investigators have found that a solution of prolycopene in petroleum ether upon contact with iodine dissolved in the same solvent forms lycopene and neolycopene within two seconds. Lycopene is the main component of the resulting isomeric mixture and is believed to have the completely *trans* structure of 6,7-8,9-10,11-12,13-14,15-16,17-18,19-20,21-22,23-24,25-26,27-*trans*-2,6,10,14,19,23,27,31-octamethyldotriacontatridecaene-2,6,8,10,12,14,16,18,20,22,24,26,30. This assignment corresponds to less overlapping of hydrogen atoms and methyl groups than is probably present in the highly *cis*-structured prolycopene and in several "bond planar" intermediates advanced mainly on mathematical grounds.



PROLYCOPENE



LYCOPENE

The methylcyclopentane and cyclohexane equilibrium has been investigated with the aid of Raman spectra measurements by S. Mizusima, Y. Morino, and R. Huzisiro [*J. Chem. Soc. Japan*, **62**, 587-591 (1941); *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **38**, No. 1034, 401-408 (1941) (in English)]. Aluminum chloride with water was used to convert the cyclohexane into equilibrium mixtures containing 12.6 per cent of methylcyclopentane at 30° or 26.5 per cent at 78.5°. The corresponding entropy change at 25° was calculated to be 9.2 ± 1.2 entropy units.

Two instances of the formation of spiro[4.5]decenes by cyclization in the presence of sulfuric acid of 84 per cent concentration have been

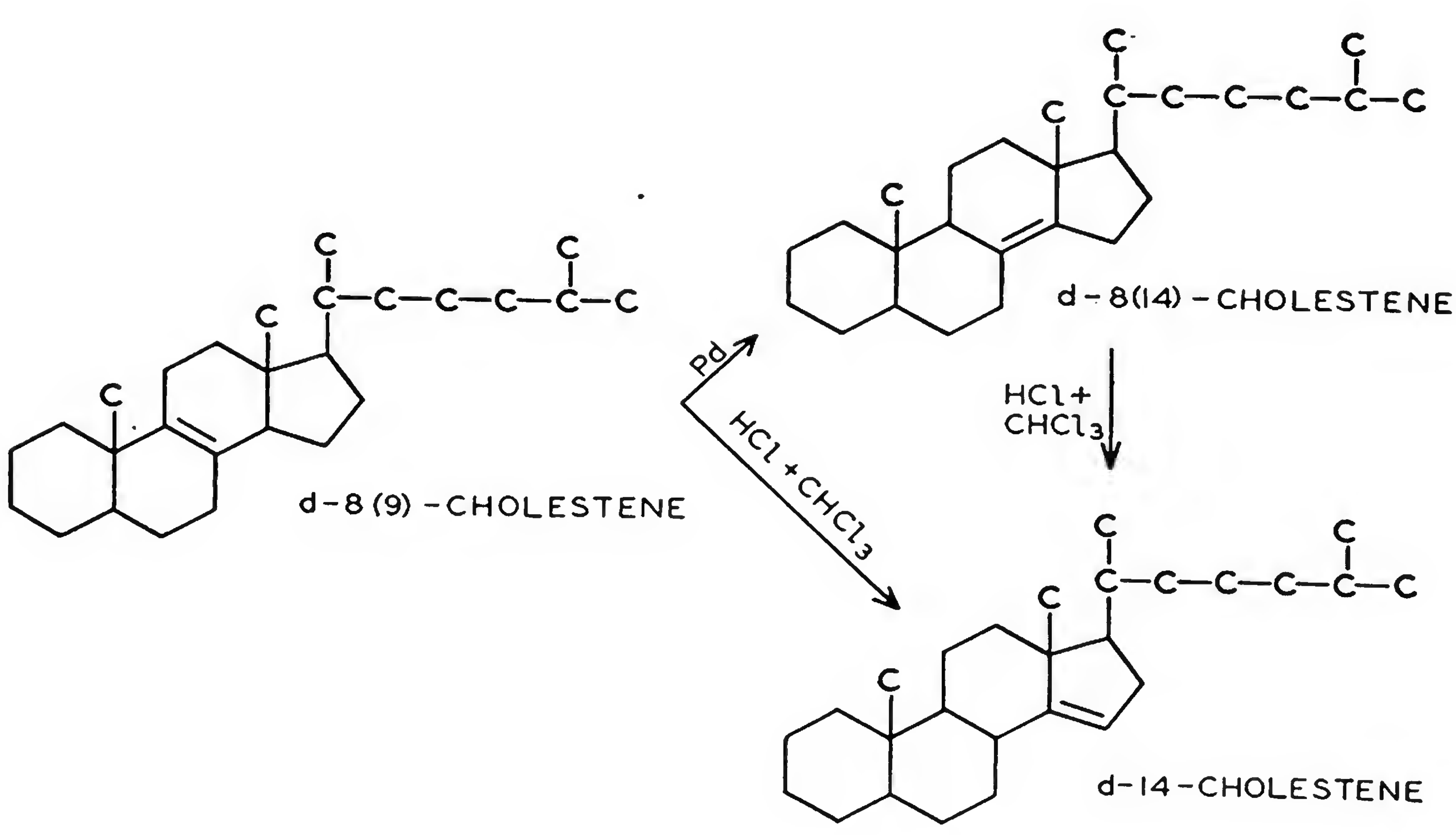
reported by C. S. Marvel and L. A. Brooks [*J. Am. Chem. Soc.*, **63,** 2630-2632 (1941)]. Treatment of a $C_{10}H_{16}$ (b.p. 172-175°, $n_D^{20} = 1.4655$) having the presumable structure of 1-(3-butenylidene)cyclopentane or 1-(3-butenyl)cyclopentene-1 gave an unsubstituted spiro[4.5]decene with unlocated double bond (there are 4 possibilities). Similarly, a $C_{11}H_{18}$ (b.p. 186-189°, $n_D^{20} = 1.4595$) presumably having the structure of 1-(3-butenylidene)-3-methylcyclopentane or 1-(3-butenyl)-3-methylcyclopentene-1 yielded a 2-methylspiro[4.5]decene with unlocated double bond (there are more than 4 possible structures).

Papers I and II of L. A. Goldblatt and S. Palkin on the vapor-phase thermal isomerization of α- and β-pinenes, originally presented before the Division of Organic Chemistry of the American Chemical Society, St. Louis Meeting, April 7-11, 1941, have been published in full [*J. Am. Chem. Soc.*, **63,** 3517-3522 (1941)]. The purified pinenes used in their investigation had the following properties:

$$d\text{-}\alpha\text{-pinene} \quad [\alpha]_D = +32.06°, \ D_4^{20} = 0.8600, \ n_D^{20} = 1.4645;$$
$$l\text{-}\beta\text{-pinene} \quad [\alpha]_D = -21.80°, \ D_4^{20} = 0.8712, \ n_D^{20} = 1.4782.$$

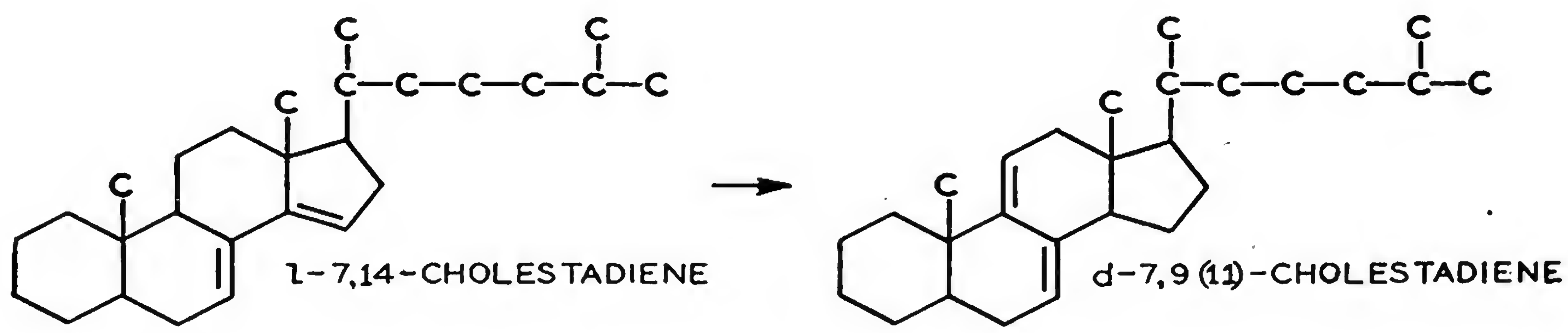
The *d*-α-pinene had a low specific rotation, indicating the presence of either some *l*-α-pinene or a terpene of very low rotatory power.

An article of Y. R. Naves and E. Perrottet [*Helv. Chim. Acta*, **24,** 789-804 (1941)] claims that caryophyllene from oil of cloves is just one chemical individual. It has two double bonds (not conjugated) distributed in the ring and as an "isopropylidene" group. The ring cannot have 7 carbon atoms, in the opinion of these investigators. They have succeeded in isomerizing tetrahydrocaryophyllene at room temperature in the presence of 50 per cent of its weight in aluminum chloride for 72 hours.

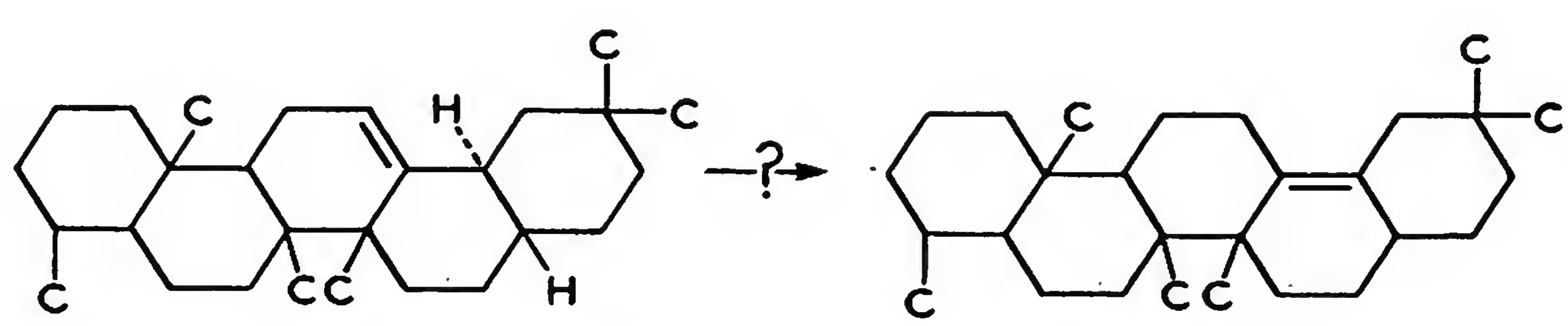


d-8(9)-Cholestene was isomerized to 90 per cent of *d*-8(14)-cholestene when subjected to a palladium catalyst in the presence of ethyl acetate and hydrogen, but formed 42 per cent of *d*-14-cholestene besides a cholestanol when dry hydrogen chloride was passed through its solution in chloroform at 0°, according to J. C. Eck and E. W. Hollingsworth [*J. Am. Chem. Soc.*, **63,** 2986-2990 (1941)]. *d*-14-Cholestene was produced to the extent of 30 per cent when a chloroform solution of *d*-8(14)-cholestene was treated with hydrogen chloride gas. (Structures on p. 429.)

l-7,14-Cholestadiene, $[\alpha]_D^{21} = -93.2°$, yielded 48 per cent of an isomer with $[\alpha]_D^{24} = +27.3°$, probably *d*-7,9(11)-cholestadiene, besides a maleic anhydride adduct, when heated under reflux with maleic anhydride in the presence of toluene for 10 hours in the work of J. C. Eck and E. W. Hollingsworth [*J. Am. Chem. Soc.*, **64,** 140-144 (1942)]. The instability of *l*-7,14-cholestadiene was also indicated by a lowered specific rotation, $[\alpha]_D = -69°$, upon repeated recrystallization.



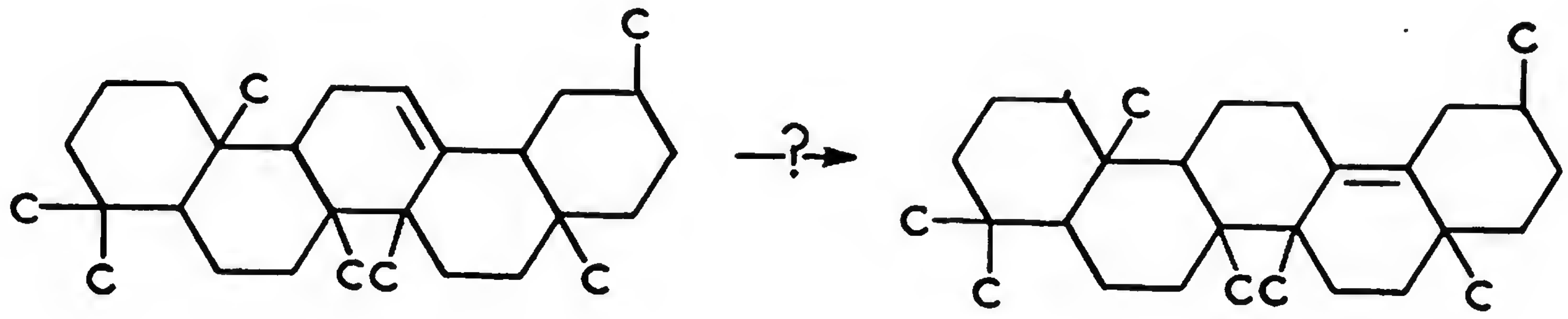
Further work on isomerizations of the pentacyclenes has been conducted by P. Bilham and G. A. R. Kon [*J. Chem. Soc.*, **1941, 552-561**]. These investigators have found that *d-trans*-norhederabetulene, which is apparently a lower homolog of *d*-$\Delta^{12,13}$-oleanene, is isomerized to "*d*-norhederabetulene-III" when boiled with acetic containing hydrochloric acid and amalgamated zinc:



d-TRANS-NORHEDERABETULENE d-NORHEDERABETULENE-III

The proposed structures are based upon the probable identity of deoxyquillaic and echinocystic acids, which calls for a *d*-4a,14b-*trans*-2,2,6a,-6b,9,12a-hexamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-eicosahydropicene structure for *d-trans*-norhederabetulene and a *d*-2,2,-6a,6b,9,12a-hexamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,-14-eicosahydropicene structure for "*d*-norhederabetulene-III." This formulation provides another explanation of the isomerizations and struc-

tures of the *cis* and *trans* forms of $\Delta^{12,13}$-oleanene discussed in the Pentacyclenes section of Chapter V, namely, the conversions of d-4a,14b-*cis*- and *d*-4a,14b-*trans*-2,4a,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,-8,8a,9,10,11,12,12a,12b,13,14b-eicosahydropicenes into *d*-2,4a,6a,6b,9,9,-12a-heptamethyl-1-2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14-eicosahydropicene:

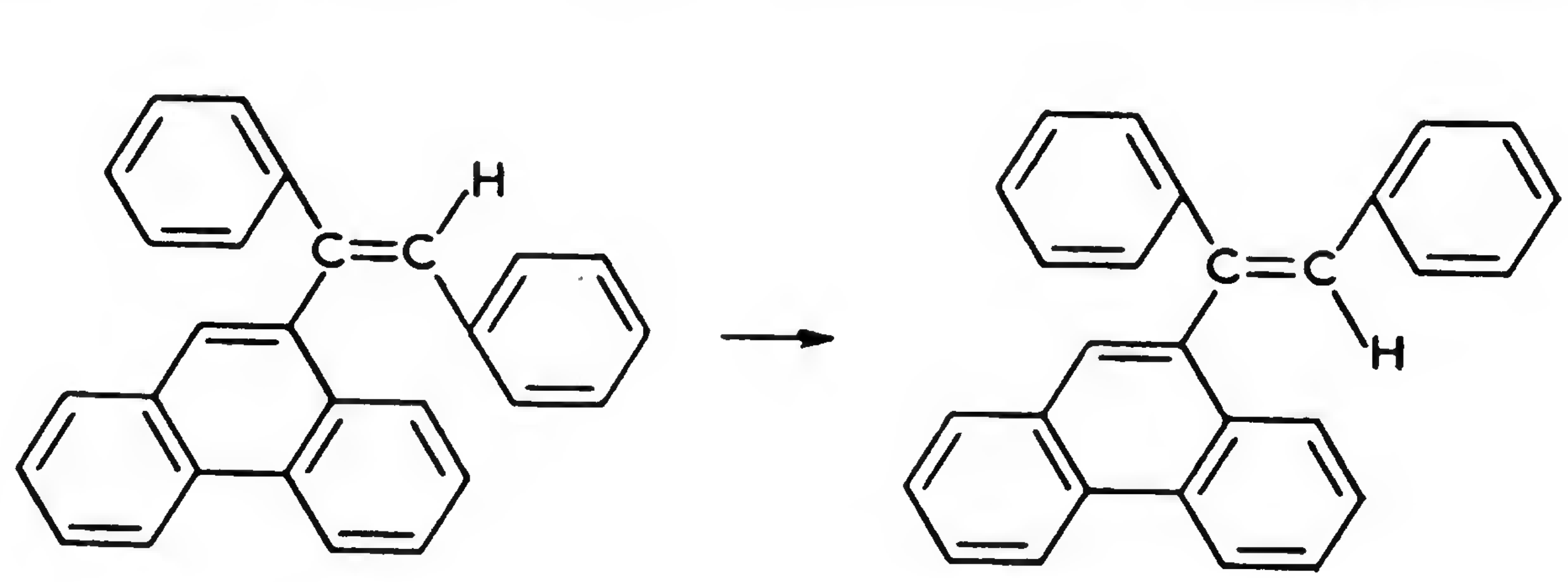


d-$\Delta^{12,13}$-OLEANENE

d-2,4a,6a,6b,9,9,12a-HEPTAMETHYL-EICOSAHYDROPICENE

The action of aluminum chloride on polyalkylbenzenes at 70-75° has been studied by D. Nightingale and F. Wadsworth [*J. Am. Chem. Soc.*, 63, 3514-3517 (1941)]. They report that 1,2,3,5- and 1,2,4,5-tetramethylbenzenes, the 1,2,4- and 1,3,5-triethylbenzenes, and the 1,2,3,5- and 1,2,4,5-tetraethylbenzenes are pairs of hydrocarbons exhibiting partial reversibility in direction of isomerization. 1,2,3,4-Tetramethylbenzene and 1,2,3,4-tetraethylbenzene yielded the corresponding 1,2,3,5- and 1,2,4,5-tetralkylbenzene isomers, with little if any of the original 1,2,3,4-hydrocarbon. These results are of interest in the interpretation of Friedel-Crafts alkylations of polyalkylbenzenes.

1,2-*Trans*-diphenyl-1-(9-phenanthryl)-ethylene (*i.e.*, 1-phenyl-(*cis*-1-[9-phenanthryl]-2-phenyl)-ethylene, m.p. 140°) underwent an isomerization to 1,2-*cis*-diphenyl-1-(9-phenanthryl)-ethylene (*i.e.*, 1-phenyl-(*trans*-1-[9-phenanthryl]-2-phenyl)-ethylene, m.p. 166-167°) when heated under reflux for two hours with nitrobenzene containing iodine, according to F. Bergmann [*J. Am. Chem. Soc.*, 64, 69-72 (1942)]. The greater repulsion of the *cis* phenyl and phenanthryl groups as compared with two *cis* phenyl groups is an interesting phenomenon:



1,2-TRANS-DIPHENYL-1-(9-PHENANTHRYL)-ETHYLENE

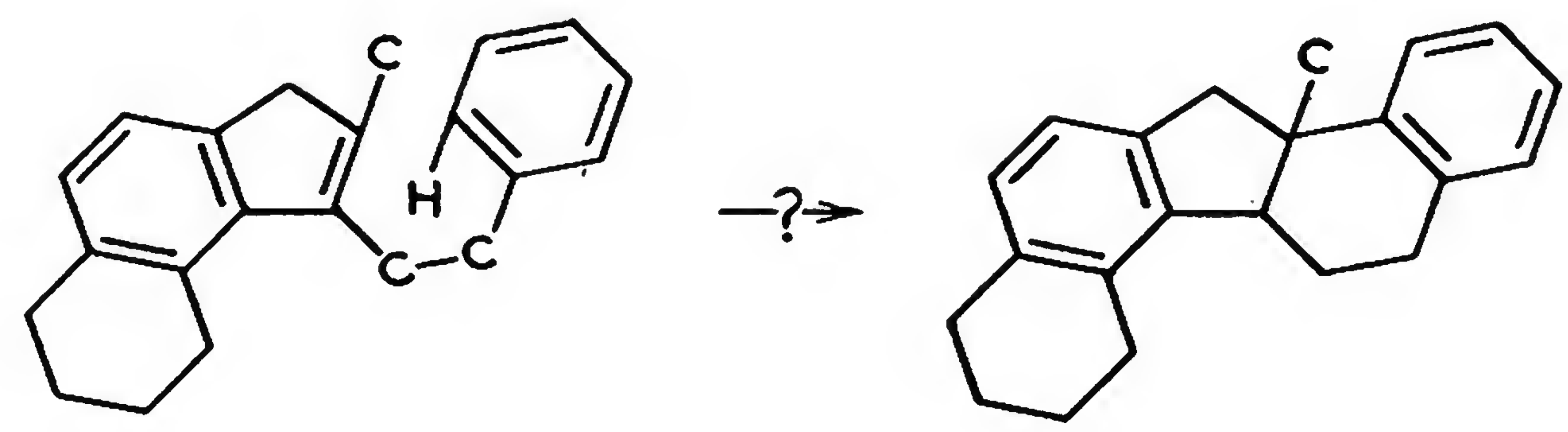
1,2-CIS-DIPHENYL-1-(9-PHENANTHRYL)-ETHYLENE

A cyclization of 2-methyl-3-(β-phenethyl)-6,7,8,9-tetrahydro-1-benz-[e]indene and/or 1-(β-phenethyl)-2-methyl-6,7,8,9-tetrahydro-3-benz-

[e]indene at 0° in the presence of aluminum chloride and carbon disulfide is indicated in the work of R. H. Martin [*J. Chem. Soc.*, **1941, 679-685**]. The structure of the product is unestablished; it may be that of 12b-methyl-1,2,3,4,6b,7,8,12b-octahydro-13-dibenzo[a,i]fluorene and/or 13a-methyl-5,6,6a,7,8,9,10,13a-octahydro-13-dibenzo[a,g]fluorene, respectively. A selenium dehydrogenation of the product at 305° for 20 hours yielded only a small amount of an aromatic hydrocarbon (m.p. 306-308°), obviously neither the expected 13-dibenzo[a,i]fluorene (m.p. 234°) nor the expected 13-dibenzo[a,g]fluorene (m.p. 172°).

2-METHYL-3-(β-PHENETHYL)-6,7,8,9-TETRAHYDRO-1-BENZ[e]INDENE

12b-METHYL-OCTAHYDRO-13-DIBENZO[a,i]FLUORENE



1-(β-PHENETHYL)-2-METHYL-6,7,8,9-TETRAHYDRO-3-BENZ[e]INDENE

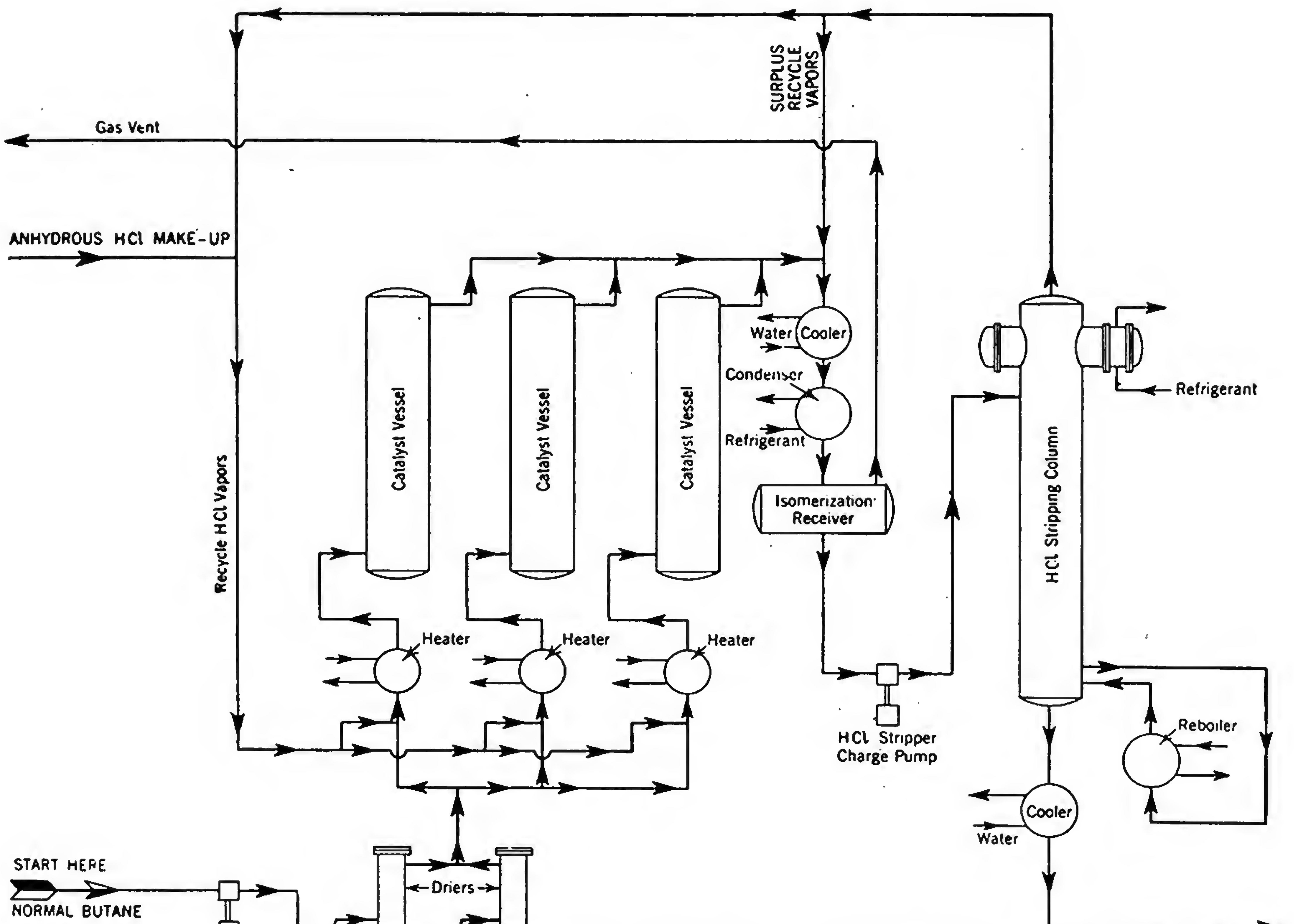
13a-METHYL-OCTAHYDRO-13-DIBENZO[a,g]FLUORENE

Applied Isomerization

The National Defense program of the United States calls for the isomerization of all available *n*-butane and *n*-pentane to obtain isobutane and isopentane for aviation gasoline. There are several commercial isomerization plants that produce these products at the present time. They utilize the Shell Oil Co., Inc., and the Universal Oil Products Co. processes. The Standard Oil Co. (Indiana) is also a process licensor [Anon., *Natl. Petroleum News,* **33**, No. 51, pp. 9 and 20 (1941)].

A number of isomerization units are being utilized for the production of isobutane from *n*-butane. A flow chart of a typical isomerization plant for converting *n*-butane into isobutane is included. Vapors of *n*-butane are passed over a granular mass containing aluminum chloride on an inorganic support. Hydrogen chloride gas is continuously recycled to the reaction zone. In single-pass operation, under the reaction conditions usually prevailing in the catalyst chambers, about 40-45 per cent of the *n*-butane input is isomerized to isobutane. With intermediary frac-

tionation, 90 per cent of the n-butane can be isomerized to isobutane. [L. J. Coulthurst, *Natl. Petroleum News,* **33,** No. 52, R-403, R-404, and R-406 (1941); *Petroleum Eng.,* **13,** No. 4, 113, 116, 118 (1942); Bulletin 0-41-13 Foster Wheeler Corp., New York. J. C. Morrell and G. Egloff, *World Petroleum,* **12,** No. 11, 70-75 (1941).]



Flow diagram of a typical Isomerization plant.

The Standard Oil Co. (Indiana) has reported that their process increases the octane number of straight-run gasoline from 65 to around 81, with 98 per cent yield in the isomerization. An aviation gasoline formerly containing 35 per cent of base stock and 65 per cent of synthetic hydrocarbons (isopentane, 2,2,4-trimethylpentane, or "alkylate") can now be produced with 60 per cent of base stock (isomerized). The 25 per cent of the enumerated synthetic hydrocarbons so conserved are available for the further production of an additional 62.5 per cent of aviation gasoline. [N.P.N. News Bureau, *Natl. Petroleum News,* **33,** No. 50, 18 (1941). Anon., *Oil Gas J.,* **40,** No. 31, 41 (1941); **40,** No. 36, 30 (1942).]

The Applied Isomerization supplement concludes with a series of interesting, representative digests of patents. Each of the patented processes involves an isomerization of hydrocarbons or of their closest deriva-

tives; but this may be preceded, masked, or supplemented by other chemical reactions. A list of United States and foreign patents on isomerization of hydrocarbons and indices of the specified charging stocks and catalysts is given, corresponding to the concluding patent digests.

Patent Number Index

Australian

106,671
113,275

Austrian

72,293
131,128

British

18,356 (1911)
18,653 (1912)
347,108
356,020
367,593
501,896
510,478
516,659
516,780
517,758
525,554
526,215
527,767
527,954
528,178
529,914
530,253
534,151
535,054
535,394
535,398
Application 12092/40

Canadian

384,317
399,051

Dutch

48,338
48,509
48,706
50,385
Application 83,778
Application 83,820
Application 86,418
Application 87,959

French

17,233
450,431
713,357
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840,717
852,114
854,936

German

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548,901
596,820
Application J. 61,782

Hungarian

Application P. 9,689

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United States

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2,105,850
2,164,334
2,175,359
2,186,022
2,199,132
2,216,131
2,216,285
2,216,470
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2,220,091
2,220,092
2,238,860
2,249,366
2,250,118
2,250,410
2,257,896
2,260,279
2,263,026
2,265,548
2,265,870
2,266,011
2,266,012
2,268,401
2,271,043

Index of Hydrocarbons or Derivatives Isomerized in the Patented Processes

Alkanes

n-Butane
British 516,659
British 516,780
British 525,554
British 527,767
British 528,178
British 535,054
British 535,394
British Application 12092/40
Canadian 399,051
Dutch 48,338
Dutch 50,385
Dutch Application 83,820
Dutch Application 86,418
French 840,717
Italian 365,253
U. S. 2,199,132
U. S. 2,216,470
U. S. 2,238,860
U. S. 2,249,366
U. S. 2,250,118
U. S. 2,257,896
U. S. 2,265,548
U. S. 2,266,011
U. S. 2,266,012
U. S. 2,268,401
U. S. 2,271,043

Isobutane
British 527,767

n-Pentane
British 526,215
British 527,954
British 528,178
British 535,054
British 535,394
Dutch 48,338
Dutch 48,706
Dutch 50,385
U. S. 2,250,118
U. S. 2,250,410
U. S. 2,265,870
U. S. 2,271,043

n-Hexane
British 527,767
British 535,054
U. S. 2,250,410
U. S. 2,268,401

n-Heptane
U. S. 2,268,401

n-Octane
British 535,054

Index of Catalytic Materials Used in the Patented Isomerizations

Digests of Patents

Australian Patents

N. V. de Bataafsche Petroleum Maatschappij, (assignee of H. Hoog), Australian Patent 106,671:

Isomerization.

Production of branched or more highly branched alkenes or alkene-containing mixtures with hydrated aluminum silicates of the permutite or zeolite type, particularly hydrated alkali aluminum silicates, at 275-500° C.

N. V. de Bataafsche Petroleum Maatschappij, (assignee of A. J. van Peski and C. A. Schuit), Australian Patent 113,275:

Isomerization.

Preventing the formation of undesirable by-products when producing saturated hydrocarbons with branched or more highly branched chains from saturated hydrocarbons boiling below 200° C. and preferably containing 4 to 6 carbon atoms by reacting at not above 200° C. in the presence of hydrogen, using aluminum halides as catalysts.

Austrian Patents

Badische Anilin- und Soda-Fabrik, Austrian Patent 72,293 of Aug. 25, 1916, British Patent 18,653 of Aug. 14, 1912, French Patent 450,431 of Jan. 19, 1912, German Patent 263,017 of July 28, 1913, and U. S. Patent 1,102,655 of July 7, 1914:

Production of isopentenes and their derivatives.

n-Pentenes are converted into isomeric alkenes, especially 2-methylbutene-2, by heating to elevated temperatures, in the presence of catalysts. Instead of *n*-pentenes, substances yielding it may be used.

n-Pentenes are produced from monochloro-*n*-pentane by passage over lime at elevated temperature. These pentenes give 2-methylbutene-2 when passed over calcined alumina at 450° C.; the hexenes from monochloro-*n*-hexane yielded a distillate which upon treatment with concentrated aqueous hydrogen chloride gave 3-chloro-3-methylpentane. 2-Methylbutene-2 is produced by passing over heated alumina the alcohol derived from methyl-*n*-propyl ketone. [*Chem. Zentr.*, **1913,** II, 729; *Chem. Abs.*, **8,** 1331 (1914); **8,** 553 (1914); **11,** 870 (1917); Friedlaender's Fortschritte der Teerfarbenfabrikation, **11,** 810-811 (1915).]

Schering-Kahlbaum A.-G., Austrian Patent 131,128 of March 11, 1931 (July 15, 1923), British Patent 367,593 of Feb. 25, 1932, French Patent 713,357 of March 16, 1931, German Patent 548,901 of March 21, 1930, Swiss Patent 153,193 of March 9, 1931:

Process for the preparation of menthene-3.

Menthene-1 is heated to a high temperature (above 300° C.) in the presence of a catalyst such as pumice stone, copper, or a copper phosphate. Menthene-3 is separated by fractionation from the mixture of isomeric menthenes formed [*Chem. Abs.*, **26,** 1626, 4069 (1932); *Chem. Zentr.*, **1932,** I, 3916; Friedlaender's Fortschritte der Teerfarbenfabrikation, **18,** 581-582 (1933).]

British Patents

Badische Anilin- und Soda-Fabrik, British Patent 18,356, Aug. 14, 1911:

2-Methylbutene-2, the 3-methylbutadiene-1,2, the 2-methylbutadiene-1,3, and halogenisopentanes.

Isoprene is produced by monohalogenating isopentane, removing hydrogen halide, converting the resulting 2-methylbutene-2 into a dihalogenisopentane, then removing 2 mols of hydrogen halide by means of a catalytic agent such as barium chloride or alumina. If a mixture of isoprene and 3-methylbutadiene-1,2 results, the latter is converted into isoprene by the catalytic action of alumina or a compound containing it. [*Chem. Abs.*, **7,** 425 (1913).]

I. G. Farbenindustrie A.-G., British Patent 347,108, Jan. 16, 1930:

Rubber isomerization.

Products which when vulcanized have good wearing qualities are obtained from rubber which is treated in suspension or solution at temperatures below 100° C. with organic-inorganic oxonium compounds, free from aldehyde groups and phenolic hydroxyl groups, preferably with exclusion of oxygen and suitably in the presence of inert organic solvents such as benzene. The oxonium compounds used may be obtained from aluminum halides, stannic chloride, concen-

trated sulfuric acid and the halides of carboxylic acids such as acetic anhydride, acetyl or phthalyl chlorides or phosgene or organic oxygen compounds such as ethers. [*Chem. Abs.*, **27,** 448 (1933).]

Schering-Kahlbaum A.-G., British Patent 356,020, Oct. 24, 1930:

α-Pinene.

Nopinene or an oil containing it is heated in the presence of a catalyst comprising an inert porous carrier such as porous pottery, artificial zeolitic material or fuller's earth. [*Chem. Abs.*, **26,** 5579 (1932).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 501,896, March 7, 1939:

Isomerization of alkenes.

Branched or more highly branched alkenes are obtained from non- or less-branched alkenes, *i.e.*, the products have more branch chains, by contacting alkenes with hydrated alkali aluminum silicates of the permutite or zeolite type at about 275-500° C. Gaseous or liquid alkenes, *e.g.*, butene, octene or alkene-containing mixtures such as a C_4 fraction of cracking gas or residual gas after polymerization thereof, and cracking gasoline may be treated. Products of gasoline boiling range can be used as such or as addition agents therefor, if desired, after hydrogenation. Isobutene obtained from *n*-butenes may be polymerized and hydrogenated to isoöctane. In examples, (1) a 50-50 mixture of *n*-butenes and butane is passed over granulated commercial sodium permutite at 450° with a contact time of 183 seconds, and (2) octene is similarly treated at 300° with a contact time of 1 minute. [*Chem. Abs.*, **33,** 6338 (1939).]

Standard Oil Development Co., British Patent 510,478, Aug. 2, 1939:

Motor fuels.

Polymers of the nature of motor fuels are produced from hydrocarbon mixtures the alkene component of which consists of iso and normal alkenes of 3-5 carbon atoms by subjecting the mixture to the action of sulfuric acid at elevated temperature and pressure in such a manner as to ensure substantially complete polymerization of the isoalkenes and only partial or no polymerization of the *n*-alkenes, distilling off the polymers so formed and subjecting the residue, which contains substantially no isoalkenes to the action of sulfuric acid of 60-80 per cent concentration while at 76.7-162.8° C. and under pressure sufficient to maintain the alkene in liquid condition, whereby a substantial portion of the *n*-alkenes is isomerized and polymerized, and separating the polymer so produced. [*Chem. Abs.*, **34,** 5274 (1940).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 516,659, Jan. 8, 1940:

A process for the manufacture of isobutane from *n*-butane.

Manufacture of isobutane from n-butane by contacting n-butane, preferably in the gaseous phase at temperatures below 200° C., with a catalyst. The catalyst consists of aluminum chloride mixed with or brought on to a carrier substance comprising an inorganic substance containing water which normally can only be split off at temperatures above 200° C., for example pipe clay dried at 300° C. Reaction may be carried out in the presence of small quantities of hydrogen chloride or water and elevated pressure may be used.

Texaco Development Corp., British Patent 516,780, July 7, 1938:

Preparation of alkylated hydrocarbons from n-alkanes.

Antiknock motor fuels are obtained by partly converting n-butane into isobutane in presence of a halide of aluminum, interaction of the isomerized portion with a C_4 alkene in presence of sulfuric acid or phosphoric acid, and recycling unchanged materials. [*Brit. Chem. Abs.-B*, **1940**, 265).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 517,758, Feb. 7, 1940:

A process for the manufacture of isobutane from n-butane.

A vapor phase process characterized by passage of the n-butane over a solid catalyst containing aluminum chloride on a carrier, such as pumice, at temperatures below 200° C. and contact times of 20 seconds. Hydrogen chloride or water is added.

Texaco Development Corp., British Patent 525,554, Aug. 30, 1940:

Treatment of hydrocarbons.

Alkylation of isobutane with alkenes occurs in the presence of suitable catalysts in the presence of excess isobutane. Reaction products are separated and unreacted hydrocarbons are separated into n- and isobutane, the latter of which is recycled to the alkylation; the former is isomerized, suitably in the presence of 5-30 per cent, preferably 10 per cent of catalyst (aluminum bromide, aluminum chloride or their hydrocarbon compounds) either alone or in the presence of hydrogen chloride. Temperatures up to 93.3° C. may be used for the isomerization, but room temperature is preferred.

N. V. de Bataafsche Petroleum Maatschappij, British Patent 526,215, Sept. 12, 1940:

Saturated branched-chain hydrocarbons from saturated straight-chain hydrocarbons.

Double compounds of aluminum halides (aluminum chloride, aluminum bromide, aluminum iodide, and aluminum fluoride) with aromatic hydrocarbons (particularly alkylated aromatic hydrocarbons such as butylbenzene or tripropylbenzene) are used as catalysts in the isomerization of straight-chain hydrocarbons boiling below 200° C. The reaction is carried out below 150° C. in liquid or gaseous phase

(as by bubbling the hydrocarbon through the complex compound) and a hydrogen halide (hydrogen chloride or hydrogen bromide) or an organic halide (propyl chloride or *tert*-butylchloride) may be present. Examples illustrate the isomerization of *n*-pentane.

I. G. Farbenindustrie A.-G., British Patent 527,767, Oct. 16, 1940:

Isomerization of low-molecular alkanes.

Alkanes having 4-12 carbon atoms in the molecule are isomerized by being passed at temperatures between 200° and 600° C., preferably between 350° and 500° C., at pressures above 100 atmospheres, together with hydrogen having a partial pressure of less than 5 per cent of the total pressure, over catalysts having an adsorbent or hydrogenating or dehydrogenating action. Small amounts of sulfur or sulfur compounds may be added to the hydrocarbons. The catalyst may be an oxide or sulfide of metals of periodic groups 6-8; in an example it is active carbon impregnated with ammonium thiomolybdate and dried in hot carbon dioxide.

N. V. de Bataafsche Petroleum Maatschappij, British Patent 527,954, Oct. 18, 1940:

A process for preparing saturated hydrocarbons with branched, or more highly branched chains from saturated hydrocarbons.

Saturated hydrocarbons boiling below about 160° C. and having 5 or more carbon atoms are converted into isomers with more highly branched chains by treating the initial hydrocarbons with hydrogen halide under high partial pressure of hydrogen halide so as to ensure the presence of a liquid phase, in the presence of Friedel-Crafts catalysts such as aluminum chloride, tungsten chloride, molybdenum chloride, zinc chloride, ferric chloride, beryllium chloride, stannic chloride, and the like. The temperature is below 150° C. and the partial pressure of hydrogen chloride is at least one atmosphere. (Corresponds to U. S. Patent 2,250,410 and Dutch Patent 48,706.)

Anglo-Iranian Oil Co., Ltd., (S. F. Birch and J. H. Beynon), British Patent 528,178, Oct. 24, 1940:

Improvements relating to the isomerization of *n*-alkanes.

Isomerization of *n*-butane or *n*-pentane is carried out in the presence of aluminum chloride with ferric chloride as a catalyst promoter, present in amounts up to 20 per cent of the catalyst. Hydrogen chloride may be present also. Addition of 1.7 per cent of anhydrous ferric chloride to the aluminum chloride in an experiment in which *n*-butane saturated with hydrogen chloride was treated raised the conversion of *n*-butane into isobutane from 61.1 per cent to 80.24 per cent.

N. V. de Bataafsche Petroleum Maatschappij, British Patent 529,914, Dec. 2, 1940:

Hydroaromatic cyclanes.

Non-hydroaromatic cyclanes containing alkanes are heated to temperatures below 200° C. with aluminum halides in the presence of hydrogen halides and hydrogen to secure isomerization of the non-hydroaromatic cyclanes into hydroaromatic cyclanes. It is preferable to carry out the reaction at a temperature below 100° C. Aluminum halides may be employed in the form of Gustavson compounds. [*Chem. Abs.*, **35**, 7414 (1941).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 530,253, Dec. 9, 1940:

Branched-chain hydrocarbons.

Unsaturated aliphatic hydrocarbons are hydrogenated. The mixture of saturated hydrocarbons and hydrogen thus produced is freed from carbon monoxide and sulfur compounds. Then it is isomerized by treatment with aluminum halides. The presence of hydrogen chloride or alkyl chlorides promotes the reaction. Gustavson's compounds, *i.e.*, double compounds of aluminum halides with aromatic hydrocarbons, may be used instead of aluminum chloride. [*Chem. Abs.*, **35**, 7972 (1941).]

Standard Oil Development Co., British Patent 534,151, Feb. 28, 1941:

Converting hydrocarbons.

Straight-chain hydrocarbons are converted into branched-chain alkenes having the same number of carbon atoms by passage at 320-595° and atmospheric pressure for 5-200 seconds over dehydrogenating-isomerizing catalysts. They comprise an oxide or silicate of aluminum with or without a carrier (silica gel) which has been activated by treatment with a mineral acid (phosphoric acid, hydrogen fluoride) or by addition of a Friedel-Crafts catalyst or of an oxide and/or sulfide of a periodic group 6 metal. The catalyst may also be phosphoric acid on silica gel. [*Brit. Chem. Abs.-B*, **1941**, *I*, 219.]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 535,054, March 27, 1941:

Motor fuels.

Conversion of saturated hydrocarbons boiling below 200° C. into isomeric hydrocarbons, *e.g.*, butane into isobutane, pentane into isopentane, hexane into branched-chain hexanes, octane into branched-chain octanes, and mixtures of normal hydrocarbons of straight-run gasoline into mixtures containing branched or more highly branched hydrocarbons. Aluminum halides are employed as catalysts at temperatures not exceeding 200° C., and the formation of by-products is repressed by carrying out the reaction in the presence of hydrogen under a total operating pressure greater than atmospheric. [*J. Inst. Petroleum*, **27**, 268A (1941).]

N. V. de Bataafsche Petroleum Maatschappij, British Patent 535,394, April 8, 1941:

Treatment of hydrocarbons in the liquid phase with metal halides, particularly in the isomerization of saturated hydrocarbons with straight or only slightly branched chains to hydrocarbons with branched or relatively highly branched chains. According to the invention, for example, *n*-butane can be converted into isobutane, *n*-pentane into isopentane, etc., and saturated gasolines with relatively low antiknock values into gasolines with relatively high antiknock values. [*J. Inst. Petroleum,* **27,** 269A (1941).]

Standard Oil Development Co., British Patent 535,398, April 8, 1941:

Conversion of normally liquid straight-chain alkanes into branched-chain alkanes by subjecting the former to the action of a catalyst of the aluminum chloride type and an activator for the catalyst, in the presence of free hydrogen and a light alkane gas containing a substantial amount of propane. [*J. Inst. Petroleum,* **27,** 269A (1941).]

Standard Oil Development Co., British Patent Application 12092/40:

Improvement relating to the isomerization of alkanes.

Liquid phase isomerization of *n*-alkanes or alkane fractions containing butane or heavier hydrocarbons at 4.4-148.9° C., space velocity of 0.1 to 5, with large amounts of catalyst present (at least equal to the hydrocarbon feed weight) and in the presence of 0.5 to 25 per cent of hydrogen chloride. Describes both fixed-bed and slurry-type operations with entrained powdered aluminum chloride. Discusses the use of hydrogen to suppress side reactions.

In the fixed-bed operation, granular aluminum chloride or a supported catalyst may be used, the supports mentioned being pumice, fuller's earth, kaolin, diatomaceous earth, "Filtrol," silica, alumina, and bauxite. In moving-bed operation, the spent catalyst is continuously removed and replaced by fresh granular catalyst fed from a hopper. Percolation-type reactors may be used singly or in groups, and the individuals comprising the latter may be used in series or in parallel, with optional temperature variations between the members, and with provision for using the first towers for purification of the feed stocks.

Canadian Patents

Shell Development Co., (assignee of A. J. van Peski and H. F. J. Lorang), Canadian Patent 384,317, Sept. 26, 1939:

Conversion of *n*-butene into isobutene.

A gaseous hydrocarbon mixture containing about 50 per cent each of butane and *n*-butenes is brought into contact with a solid catalyst

comprising a calcined mixture of a phosphorus oxy-acid and a solid siliceous material at about 275-325° for about 2-50 seconds. Polymerization of the butenes is substantially obviated. [*Chem. Abs.*, **34,** 1336 (1940).]

Shell Development Co., (assignee of W. F. Engel), Canadian Patent 399,051, Sept. 2, 1941:

Hydrocarbon isomerization (7 claims).

Claim 1. A process for the conversion of normal and branched-chain saturated hydrocarbons to branched and more highly branched-chain saturated hydrocarbons which comprises contacting the hydrocarbon to be treated at a temperature not greater than 200° C. with a solid catalyst essentially comprising an effective amount of anhydrous aluminum chloride and an aluminum oxide which has been previously partially dehydrated by a heat treatment at a temperature greater than 200° C. until it is capable of losing further water of hydration at higher temperatures, but is incapable of further substantial dehydration at a temperature below 200° C. [Canadian Patent Office Record, **69,** 2451 (1941).]

Dutch Patents

N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 48,338, April 15, 1940 (Application 87,201 of April 1, 1938):

Producing isoalkanes from *n*-alkanes.

Isoalkanes are produced from *n*-alkanes boiling below 100° C. by treatment with aluminum halides in the form of double compounds of aluminum halide and aromatics containing one or more alkyl groups. The temperature is below 150° C., generally room temperature, and hydrogen halide or an organic halide is added. *n*-Butane is converted into isobutane, *n*-pentane into isopentane, or a mixture of normal hydrocarbons boiling below 100° C. (*e.g.*, fractions of straight-run gasolines) into a mixture of branched-chain hydrocarbons. Reaction may be effected in either liquid or in vapor phase, and, if desired, increased pressure may be applied.

N. V. de Bataafsche Petroleum Maatschappij, (assignee of H. Hoog), Dutch Patent 48,509, May 15, 1940:

See British Patent 501,896 of March 7, 1939, and French Patent 841,004 of May 9, 1939.

N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 48,706, June 15, 1940:

Isomerization of alkanes.

Saturated straight-chain hydrocarbons containing 5 or more carbon atoms, with b.p. of 160° or less, are converted into branched-

chain saturated hydrocarbons by treatment with hydrogen halide under sufficient pressure to cause a liquid phase to be present and in the presence of Friedel-Crafts type of catalyzers. The conversion is effected at temperatures below 150° and with a partial pressure of hydrogen halide of at least one atmosphere. Especially suggested is the use of aluminum chloride and hydrogen chloride at temperatures below 100°. [*Chem. Abs.*, **35**, 1412 (1941). Cf. British Patent 527,954 and U. S. Patent 2,250,410.]

N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 50,385, May 15, 1941 (Application 89,775 of Sept. 16, 1938):

Isomerization of *n*-butane and *n*-pentane.

n-Butane or pentane is treated in the liquid phase below 200° with aluminum halide or mixtures such as aluminum chloride and *tert*-butyl chloride in the presence of hydrogen under pressure. Too high a hydrogen pressure (*e.g.*, 200 atmospheres) with pentane at 40° will prevent isomerization. [*Chem. Abs.*, **35**, 7700 (1941).]

N. V. de Bataafsche Petroleum Maatschappij, Dutch Application 83,778, Aug. 14, 1937 (Filed), Aug. 15, 1939 (Laid open):

Producing branched alkenes from *n*-alkenes.

Branched-chain alkenes are produced from *n*-alkenes by contact at elevated temperature (275-500° C.) with hydrated aluminum silicates of the permutite or zeolite type, particularly with hydrated alkaline aluminum silicate. The process is especially suitable for conversion of butane-butene mixtures. The process can be carried out under pressure, but care should be taken not to cause undesirable polymerization by too great a pressure. The lower alkenes such as butene-1 or butene-2 can be treated at higher temperatures and during a longer contact time than the higher alkenes, without danger of cracking or dehydrogenation.

N. V. de Bataafsche Petroleum Maatschappij, Dutch Application 83,820, Aug. 18, 1937 (Filed), May 15, 1940 (Opp. expired):

Isobutane from *n*-butane.

Isobutane is prepared from *n*-butane by treating the latter below 200° C., with a Friedel-Crafts type halide catalyst, such as aluminum chloride or aluminum bromide. The contact time is short enough so that isomerization is the chief reaction taking place.

N. V. de Bataafsche Petroleum Maatschappij, Dutch Application 86,418, Feb. 12, 1938 (Filed), May 15, 1940 (Opp. expired):

Isobutane from *n*-butane.

n-Butane or mixtures containing it are treated at temperatures below 200° C. with mixtures of aluminum chloride and inorganic substances that contain water normally driven off by heating to over 200° C. (*e.g.*, china clay dried at 300° C.). Atmospheric, reduced, or

elevated pressure may be used, and either liquid- or gas-phase reaction is permissible.

N. V. de Bataafsche Maatschappij, Dutch Application 87,959, May 21, 1938 (Filed), May 15, 1940 (Opp. expired):

Isomerization of alkanes.

Corresponds to French Patent 854,936 of April 27, 1940 (Published).

French Patents

Badische Anilin- und Soda-Fabrik, French Patent 17,235, Feb. 19, 1913:

Isoprene.

Addition to French Patent 440,130 of Feb. 13, 1912. Instead of 3-methylbutadiene-1,2, the 3-methylbutyne-1 may be used for making isoprene. (*Chem. Abs.*, **8**, 1022 (1914); corresponds to German Patent 268,102 of Dec. 8, 1913.

Standard Oil Development Co., French Patent 837,202, Feb. 6, 1939:

Hydrocarbons for use as motor fuel.

Unsaturated hydrocarbons of low boiling point composed mainly of *n*-alkenes are subjected to heating in the presence of isomerizing and polymerizing catalysts. Sulfuric acid may be used as catalyst and may be in the form of 60-80 per cent solution. Reaction may be effected at 77-163° C. and at elevated pressure. [*Chem. Abs.*, **33**, 7091 (1939).]

Texas Development Corp., French Patent 840,717, May 3, 1939:

Alkylated hydrocarbons.

Motor fuels of high antiknock value are prepared by transforming *n*-butane, by isomerization in the presence of aluminum halide, into isobutane and causing this to react with an alkene in the presence of a mineral acid (sulfuric acid) which gives an isoalkane of higher molecular weight than the alkene (butenes). [*Chem. Abs.*, **33**, 8983 (1939).]

N. V. de Bataafsche Petroleum Maatschappij, French Patent 852,114, Jan. 24, 1940 (Published):

Isoalkanes from *n*-alkanes.

Branched alkanes are prepared from straight-chain or less branched alkanes by treatment at temperatures below 150° C. in the presence of double compounds of aluminum halide with aromatic hydrocarbons, preferably alkylated aromatic hydrocarbons, in the presence of a hydrogen halide or an organic halide.

N. V. de Bataafsche Petroleum Maatschappij, French Patent 854,936, Jan. 29, 1940 (Issued), April 27, 1940 (Published):

Branched-chain from straight-chain hydrocarbons.

Saturated hydrocarbons boiling below 160° C. containing 5 or

more carbon atoms are treated at temperatures below about 150° C. (preferably below 100° C.) in the presence of Friedel-Crafts catalysts (preferably aluminum chloride) and under a partial pressure of hydrohalogen acid (hydrogen chloride) of at least one atmosphere. Pressure used is sufficient to keep the reaction in the liquid phase. The process is preferably carried out in the absence of water, and the Friedel-Crafts catalysts used are chlorides of Al, W, Mo, Zn, Fe^{+++}, Be, and Sn^{++++}.

German Patents

Schering-Kahlbaum A.-G., (assignee of F. Ulffers), German Patent 596,-820, May 14, 1934:

Terpenes.

In transforming terpenes, catalysts consisting of organic or inorganic acids not forming stable addition products with terpenes, or their anhydrides or salts with volatile bases, are used. Thus $(NH_4)_2WO_4$ is heated to 295° with superheated steam to form a suitable catalyst. [*Chem. Abs.*, 28, 5076 (1934).]

I. G. Farbenindustrie A.-G., German Application J. 61,782, (Laid open) Aug. 10, 1939:

Catalysts for hydrocarbon reactions.

Process for carrying out catalytic reactions using as catalysts metal sulfides completely free of oxygen, produced by treatment of metal sulfides of any origin with sulfur or oxygen-free volatile sulfur compounds. The catalysts may be sulfides of metals of the second to the eighth group, used alone, in admixture, or on carriers such as activated carbon, activated silica gel, clays, bauxite, pumice, magnesite, magnesia, chromia and the like. These catalysts are suitable for hydrogenation, cracking, decomposition of original sulfur compounds in gases to be purified, isomerization of gasoline, etc.

Hungarian Application

N. V. de Bataafsche Petroleum Maatschappij, Hungarian Application P. 9,689, (Filed) July 27, 1939, (Opp. expired) May 2, 1940:

Saturated hydrocarbons boiling below 200° C., preferably those containing 4-6 carbon atoms are converted into saturated hydrocarbons with branched chains or more highly branched chains, by treatment with aluminum halides at temperatures below 200° C. in the presence of enough hydrogen to suppress decomposition. Claim 3 specifies the presence of an activating substance such as hydrogen chloride or an alkyl halide. The hydrogen may be formed in the reaction by the action of hydrogen chloride on metals. The aluminum halide may be formed wholly or partly under the reaction conditions

by the interaction of hydrogen chloride and aluminum. The process may be operated continuously by passing vaporous or gaseous hydrocarbons over the catalyst.

Italian Patent

Texaco Development Corp., Italian Patent 365,253, July 19, 1938: Alkylated hydrocarbons.

Higher molecular weight isoalkanes, particularly antiknock gasolines, are obtained from normal hydrocarbons by conversion into isoalkanes and alkylation with alkenes. For example, *n*-butane is isomerized to isobutane with halides of aluminum, chromium or iron, especially with aluminum chloride or bromide. The isobutane is alkylated to isoöctane with butenes (*e.g.*, isobutene), diisobutene, cracked gases, liquid cracked distillates or polymer gasolines, in the presence of a mineral acid (phosphoric acid or 80-100 per cent sulfuric acid) at temperatures between −17° and +205° C., particularly at 21-38°. Corresponds to French Patent 840,717 of May 3, 1939. [*Oel u. Kohle ver. Petroleum,* **36,** S-26 (1940).]

Russian Patent

A. V. Frost, E. K. Serebriakova and D. M. Rudkovsky, Russian Patent 51,181, June 30, 1937:

Isomerization of alkenes.

Alkenes are heated to 200-400° C. in the presence of phosphoric acid, acid sulfates or phosphates of metals of the first, second, or third groups of the periodic system, or of Fe, Co, Ni, Cr, and Mn as catalysts, which may be supported on carriers. Gases or vapors may be added advantageously to the alkenes to prevent polymerization. A mixture of *n*-butenes with 2-4 per cent of isobutene soluble in 68 per cent sulfuric acid, is passed at 200-400° C. over chamotte impregnated with phosphoric acid. The reaction product contains 15-40 per cent of isobutene soluble in 68 per cent sulfuric acid [*Chem. Zentr.,* **1938,** II, 592].

U. S. Patents

H. Meerwein, F. Ülffers, R. Erbe, F. Aichner, and W. Klaphake, (assignors to Schering-Kahlbaum A.-G.), U. S. Patent 1,985,792, Dec. 25, 1934:

Catalysts for conversion of terpenes, such as in producing camphene from nopinene and α-pinene.

A base such as sodium hydroxide or ammonia is caused to react with an inorganic acid, inorganic "complex" inorganic acid or inorganic-organic "complex" acid such as tungstic acid or phosphotungstic

acid which combines with terpenes, if at all, only "reluctantly" or with a salt of such an acid which has an acid reaction and the base is subsequently removed from the salt formed (as by acid or evaporation) and the product is converted into a hydrate of high catalytic efficiency. Numerous examples are given. [*Chem. Abs.*, **29**, 1104 (1935).]

A. J. van Peski, (assignor to Shell Development Co.), U. S. Patent 2,105,850, Jan. 18, 1938:

Process for the reforming of gasoline distillate (11 claims).

Claim 1. In the process of reforming gasoline distillates to improve their antiknock rating, the steps comprising contacting a gasoline distillate of low antiknock rating at a reforming temperature between 225° and 500° C. with a reforming catalyst in the presence of a small quantity of a tertiary alkyl halide for a time sufficient to effect reforming without forming a substantial amount of gas.

E. M. Marks, (assignor to Atlantic Refining Co.), U. S. Patent 2,164,334, July 4, 1939:

Antiknock motor fuel.

Gasoline of high antiknock value is produced by chlorinating naphtha having a relatively low antiknock value to produce chlorinated naphtha containing about 5-20 per cent of chlorine, heating the chlorinated naphtha to about 200-450° C. under substantial superatmospheric pressure to isomerize it, then heating at substantially atmospheric pressure to about 200-240° C. in the presence of a dechlorinating agent.

E. A. Ocon, U. S. Patent 2,175,359, Oct. 10, 1939:

Reducing and recovering branched chain aliphatics.

The straight-chain aliphatic hydrocarbons that occur in natural gas and crude petroleum, or the oxygenated derivatives of these hydrocarbons are transformed to branched chain aliphatics by a multistage process. Oxygenated derivatives such as alcohols produced by treating cracking gas with concentrated sulfuric acid at 32.2° C., to remove mainly isoalkenes and hydrolyzing, are passed with suitable proportions of reducing gas (*e.g.*, water gas or water gas enriched with hydrogen) over a catalyst with relatively high hydrogenating and low dehydrating activity, at 315.6-482.2° C. at superatmospheric pressure, with a space velocity of 75-200 cu. ft. per hr. per cu. ft. of catalyst. The catalyst may be zinc oxide, chromia, cuprous oxide, manganous oxide, etc., singly or mixed, and in the presence of an alkaline compound (potassium carbonate, potassium hydroxide, alkali salts of aliphatic acids and the like), and may be on an inert carrier. Suggested catalyst mixtures are cobalt-alumina; molybdena-alumina, etc.; it is best to avoid a catalyst with too strong hydrogenating tendencies, such as nickel. Products from the *hydro-isomerization zone*

are fractionated into an overhead of low-boiling hydrocarbons, and a reflux containing unconverted alcohols. A heavy unvaporized hydrocarbon fraction may be removed from the catalytic zone. The low-boiling iso-aliphatics may be hydrogenated or polymerized for aviation fuel ingredients. Similar to British Patent 535,210, April 2, 1941 (E. A. Ocon).

M. M. Holm and W. H. Shiffler, (assignors to Standard Oil Co. of California), U. S. Patent 2,186,022, Jan. 9, 1940:

A catalyst of character similar to U. S. Patent 2,186,021 (comprising a thin film of active polymerizing agent such as phosphoric acid carried on the surface of particles of a nonporous inert solid such as quartz) is used to effect reactions such as isomerization, without polymerization. [*Chem. Abs.*, **34**, 2862 (1940).]

C. M. Hull, (assignor to Standard Oil Co. of Indiana), U. S. Patent 2,199,132, Apr. 30, 1940:

Catalytic process comprising polymerization, isomerization and dehydrogenation.

The patent relates to a process for converting C_4 hydrocarbons resulting from a cracking operation into motor fuel. The hydrocarbons are first polymerized using phosphoric acid catalyst to convert the butenes. The *n*-butane stream is then catalytically isomerized using an aluminum halide-hydrogen halide catalyst. The isobutane formed is treated with a dehydrogenating catalyst and the isobutene formed recycled to the polymerization step. The polymers formed are hydrogenated to produce octanes.

M. Pier and K. Schoenemann, (assignors to I. G. Farbenindustrie A.-G.), U. S. Patent 2,216,131, Oct. 1, 1940:

Polynuclear carbon compounds.

A bituminous material is heated under pressure with hydrogen to effect substantial hydrogenation and formation of substantial amounts of polynuclear carbon compounds and cyclic carbon compounds of the hydroaromatic series, and the fraction of the product that contains the polynuclear and cyclic compounds is heated in the presence of an isomerization catalyst to effect isomerization of the polynuclear and cyclic compounds. [*Chem. Abs.*, **35**, 753 (1941).]

C. L. Thomas and H. S. Bloch, (assignors to Universal Oil Products Co.), U. S. Patent 2,216,285, Oct. 1, 1940:

Isomerization of *n*-Butene (8 claims).

A process for converting *n*-butenes into isobutene which comprises contacting said *n*-butenes with a synthetically prepared composite mass of silica, alumina, and thoria at a temperature in the approximate range of 371-593° C. Results obtained at 450-505° C. are disclosed, indicating up to 20.5 per cent isomerization of the *n*-butenes.

W. E. Forney, (assignor to Power Patents Co.), U. S. Patent 2,216,470, Oct. 1, 1940:

Catalytic conversion of natural gas gasoline, etc., to obtain improved antiknock character.

An arrangement of apparatus is described, and a process of catalytically converting an alkane containing from 3 to 4 carbon atoms to the molecule into a mixture of hydrocarbons having a substantially higher molecular weight, which comprises carrying out the process in the absence of added hydrocarbons of other type and hydrogen at a superatmospheric pressure of from 27.22 to 40.83 atmospheres, preheating the aliphatic hydrocarbon to be converted and mixing it with a relatively small proportion of a solid catalytic metallic salt which is adapted to catalyze isomerization and alkylation reactions, passing the resulting mixture in a stream of restricted cross-section through a long heating zone in the first part of which the mixture is heated to at least 398.9° C. and in the latter part of which the temperature is substantially maintained and raised to approximately 454.4° C., discharging the resulting heated mixture into an enlarged reaction zone in which intimate contact is maintained between the hydrocarbons and the catalytic material, passing the mixture into a separator in which the catalytic material is separated from the resulting converted hydrocarbon, and recovering the condensable products resulting from the conversion reactions. Catalytic salts used may be the Fe, Al, Cu, Zn, Mo, Cr, Mn, or Ni salts of phosphoric, sulfuric, hydrochloric, silicic, or boric acids. [*Chem. Abs.*, **35,** 1215 (1941).]

B. L. Evering and G. G. Lamb [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,220,090, Nov. 5, 1940:

Conversion of hydrocarbon products (6 claims).

In a process for converting substantial amounts of the straight-chain alkanes in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, isobutane, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely isobutane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial part of the straight-chain alkanes in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

B. L. Evering and G. G. Lamb [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,220,091, Nov. 5, 1940:

Conversion of hydrocarbon products (7 claims).

In a process for converting substantial amounts of the straight-chain alkanes in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons, whereby a motor fuel fraction having a relatively high antiknock value is obtained, the steps comprising contacting in a reaction zone an admixture of said petroleum naphtha, propane, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely propane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial part of the straight-chain alkanes in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

B. L. Evering and G. G. Lamb [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,220,092, Nov. 5, 1940:

Conversion of hydrocarbon products (8 claims).

In a process for converting substantial amounts of the straight-chain alkanes in a low antiknock straight run petroleum naphtha into saturated branched-chain hydrocarbons whereby a motor fuel fraction having a relatively high antiknock value is obtained, the step comprising contacting in a reaction zone an admixture of said petroleum naphtha, at least one normally gaseous hydrocarbon having at least two carbon atoms per molecule, a conversion catalyst selected from the group consisting of aluminum chloride, aluminum bromide and their hydrocarbon complexes, and a halogen-containing promoter for said catalyst, the reacting hydrocarbon gases present being largely heavier than methane and substantially free of unsaturated hydrocarbons, at an elevated temperature and pressure sufficient to convert a substantial part of the straight-chain alkanes in said petroleum naphtha into saturated branched-chain hydrocarbons without substantial formation of hydrogen and methane, withdrawing the products from said reaction zone and separating said motor fuel fraction from said products.

L. C. Kemp (assignor to The Texas Co.), U. S. Patent 2,238,860, April 15, 1941:

Motor fuel.

An arrangement of apparatus is described, and a process for the conversion of natural gasoline hydrocarbons into high-octane motor fuel

hydrocarbons which involves fractionating natural gasoline to separate therefrom fractions respectively rich in *n*-butane and isobutane and to produce a fraction comprising mainly hydrocarbons of higher molecular weight than butane, subjecting the *n*-butane fraction to isomerization to produce isobutane, subjecting the fraction comprising hydrocarbons of higher molecular weight than butane to thermal conversion to form alkenes including normally gaseous alkenes, fractionating the products of conversion to separate therefrom a fraction comprising C_3 and C_4 hydrocarbons, including alkenes, and a high-boiling fraction comprising motor-fuel hydrocarbons of relatively high octane rating, subjecting the C_3 and C_4 fraction to alkylation with the isobutane, and subjecting the products of alkylation to fractionation to separate therefrom a fraction comprising hydrocarbons suitable as aviation motor fuel of high octane value. [*Chem. Abs.*, **35**, 5300 (1941).]

A. J. van Peski and G. H. Visser (assignors to Shell Development Co.), U. S. Patent 2,249,366, July 15, 1941:

Production of isobutane.

n-Butane is treated with aluminum halide (aluminum chloride or aluminum bromide) and hydrogen halide in the presence of at least 3 atmospheres pressure of hydrogen halide and temperatures of 60-120° C. when vapor phase isomerization is carried out, or at temperatures below 100° C. when the butane is treated in the liquid phase. The catalyst may be employed in either solid or liquid phase.

W. C. B. Smithuysen (assignor to Shell Development Co.), U. S. Patent 2,250,118, July 22, 1941:

Isomerization of hydrocarbons.

Isomerization of normal saturated hydrocarbons with 4 to 9 carbon atoms by contacting at 20-140° C. with a preformed complex compound of aluminum halide (aluminum chloride) and an alkylated aromatic hydrocarbon, in the presence of hydrogen halide (hydrogen chloride). (Corresponds to Dutch Patent 48,338 and French Patent 852,114).

A. J. van Peski (assignor to Shell Development Co.), U. S. Patent 2,250,410, July 22, 1941:

Catalytic treatment of hydrocarbons.

A normally liquid *n*-alkane with at least 5 carbon atoms per molecule, and boiling not above 160° C. is converted into the isoalkane by contact at 20-150° C. with an acid-acting halide catalyst (halides of Al, Zn, Fe, As, Sb, Mo, W, etc.) for a time not exceeding 17 hours under a pressure of hydrogen halide equivalent to 3-20 atmospheres when measured at 20° C. (Corresponds to British Patent 527,954 and Dutch Patent 48,706).

W. A. Yarnall (assignor to The Texas Co.), U. S. Patent 2,257,896, Oct. 7, 1941:

Catalytic treatment of hydrocarbons.

Petroleum hydrocarbons, particularly gaseous alkanes such as *n*-butane, are isomerized by treating them with a solution of a non-gaseous halide of polyvalent metal or metalloid in anhydrous liquefied hydrogen halide under pressure higher than the vapor pressure of the hydrogen halide at the temperature of treatment to maintain liquid conditions. The metal or metalloid halides mentioned are those of Be, B, Al, Si, P, S, Ti, V, Cr, Fe, Ni, Co, Cu, Zn, Ga, Ge, As, Se, Zr, Mo, Ag, Cd, In, Sn, Sb, Te, Ce, Ta, W, Hg, Pb, Bi, and U. *n*-Butane is converted into isobutane at −1.11 to +51.7° C. using aluminum chloride dissolved in hydrogen halide.

E. L. d'Ouville, B. L. Evering, and A. G. Oblad [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,260,279, Oct. 21, 1941:

Branched-chain hydrocarbons from hydrocarbon mixtures.

Effective conversion of *n*-alkanes into isoalkanes by treatment with aluminum chloride requires a feed stock substantially free of aromatics. A mixture of alkanes with naphthenes and/or aromatics, such as a naphtha, is subjected first to an aromatization step if it contains naphthenes, to convert the latter into aromatics, next to an extraction to selectively remove the aromatics so that the stock contains not more than 2 volume per cent of aromatics, and the raffinate is isomerized. The aromatization step may be carried out at 260-537.8° C., preferably 454.4° C., under hydrogen pressure over suitable catalysts (for example, 90 Al_2O_3:10 Cr_2O_3); hydrogen is removed in a gas separator, and the gas-free stock is extracted with a selective solvent which may be liquefied sulfur dioxide, an aluminum chloride-hydrocarbon complex, or other solvents; the raffinate is isomerized with aluminum halide catalyst in the presence of an activator (suitably aluminum chloride with hydrogen chloride), or with aluminum chloride-hydrocarbon complex. In the isomerization step hydrogen may be introduced. The removal of aromatics may be effected by alkylation with low molecular weight alkenes, followed by distillation, instead of using solvent extraction. The broadest claims cover treating a naphtha containing straight-chain alkanes and aromatics to give a mixture containing alkanes and not more than 2 per cent of aromatics and subjecting this to isomerization with aluminum halide and an activator yielding hydrogen halide.

M. H. Arveson [assignor to Standard Oil Co. (Indiana)], U. S. Patent 2,263,026, Nov. 18, 1941:

Combination dehydrogenation and isomerization process.

This patent relates to a process which comprises subjecting alkane-

containing gasoline to the action of a dehydrogenation catalyst at a temperature of about 398.9 to 482.2° C. and then conducting the alkenes and hydrogen vapors from said step to a second zone wherein the alkenes undergo isomerization in the presence of a catalyst comprising phosphoric acid or aluminum oxide. The dehydrogenation catalyst may comprise an oxide of chromium or of molybdenum.

The claims cover the catalysts mentioned and reaction pressures of about 0.68 to 3.4 atmospheres.

G. C. A. Schuit (assignor to Shell Development Co.), U. S. Patent 2,265,-548, Dec. 9, 1941:

Process for the production of isobutane (8 claims).

Claim 1. In a process for the production of isobutane by the catalytic isomerization of *n*-butane wherein the isomerization is effected by contacting *n*-butane with an aluminum halide isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect the isomerization of *n*-butane as the predominant reaction, the improvement which comprises effecting the isomerization in the presence of an aluminum halide catalyst containing a metal which reacts with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

G. C. A. Schuit (assignor to Shell Development Co.), U. S. Patent 2,265,-870, Dec. 9, 1941:

Isomerization of hydrocarbons (9 claims).

Claim 1. In a process for the isomerization of hydrocarbons wherein a saturated hydrocarbon containing at least five carbon atoms is contacted with an aluminum chloride isomerization catalyst and a hydrogen halide promoter under isomerization conditions to effect isomerization as the predominant reaction, the improvement which comprises effecting the isomerization in the presence of an aluminum chloride catalyst containing sufficient metallic aluminum to react with a portion of the hydrogen halide promoter, whereby undesirable side reactions are repressed.

E. L. d'Ouville and B. L. Evering [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,266,011, Dec. 16, 1941:

Production of isobutane from n-butane (11 claims).

This patent relates to the production of isobutane by contacting a mixture of propane, *n*-butane, and an aluminum halide catalyst at a temperature of about 121.1° to 287.8° C., preferably 176.7° to 246.1° C., and a pressure of about 34.0 to 408.3 atmospheres, with the addition of an activator which may be a hydrogen halide or a compound yielding hydrogen halide under the reaction conditions.

In the isomerization of *n*-butane by treatment with an aluminum halide catalyst effective in converting *n*-butane into isobutane and

an activator for said catalyst at a temperature in the range from about 121.1° C. to about 287.8° C., the improvement which comprises carrying out said treatment in the presence of about 10 to 50 per cent of propane by weight based on the *n*-butane undergoing treatment.

E. L. d'Ouville and B. L. Evering [assignors to Standard Oil Co. (Indiana)], U. S. Patent 2,266,012, Dec. 16, 1941:

Production of branched-chain alkanes (14 claims).

This patent relates to the production of branched-chain alkanes from normally liquid hydrocarbons and more particularly to the conversion of normally liquid saturated hydrocarbons and mixtures thereof containing a large proportion of straight-chain alkanes into products consisting predominantly of branched-chain alkanes.

The process of converting a substantial portion of the straight-chain alkanes in a substantially saturated normally liquid hydrocarbon fraction into branched-chain alkanes which comprises contacting an admixture of said hydrocarbon fraction, an aluminum halide catalyst effective in causing said conversion, an activator for said catalyst, free hydrogen and an alkane gas containing a substantial amount of propane in a reaction zone maintained at a temperature in the range from about 148.9° C. to about 287.8° C. and a pressure in the range from about 34.0 to 408.3 atmospheres, said propane being present in said reaction zone in an amount lying in the range from about 10 per cent to about 35 per cent by weight based on the straight-chain alkanes present.

C. N. Kimberlin, Jr. (assignor to Standard Oil Development Co.), U. S. Patent 2,268,401, Dec. 30, 1941:

Isomerization process (3 claims).

A process for isomerizing alkanes in the presence of a Friedel-Crafts type catalyst (aluminum chloride) and a hydrogen halide (hydrogen chloride) as activator. Small amounts of an alkyl halide (carbon tetrachloride) are added to the reaction mixture as required to make up for losses of the catalyst activator during the process.

A. J. van Peski (assignor to Shell Development Co.), U. S. Patent 2,271,043, Jan. 27, 1942:

Isomerization of hydrocarbons (9 claims).

This invention relates particularly to the catalytic conversion of *n*-butane and *n*-pentane into isobutane and isopentane, respectively. Nine examples are submitted to illustrate various aspects of the invention.

"The isomerization is preferably effected with the aid of an aluminum halide such as aluminum chloride or aluminum bromide. Although the aluminum halides are, in general, the most practical and efficient catalysts, such other acid-acting halide catalysts as exert a

catalytic influence on the isomerization of hydrocarbons, *e.g.*, the halides of Be, Zn, Zr, Nb, Ta, Sb, and B, may also, if desired, be employed. Exceptionally suitable catalyst combinations are mixtures of an aluminum halide with a free metal of the group consisting of Al, Be, Mg, Zn, Cu, and Fe.

"The catalysts are preferably employed in the solid state in any suitable form such as granules, powder, or pellets of the desired size, preferably deposited on or mixed with a suitable solid supporting material. Particularly effective catalysts are produced when aluminum chloride is supported in or intimately mixed with one of the various siliceous and/or aluminous materials of natural or synthetic origin which contain an appreciable amount of firmly-bound water. Suitable materials of the category are, for example, the naturally-occurring minerals and clays, such as pipe clay, bauxite, fuller's earth, bentonite, kaolin, Florida earth, meerschaum, infusorial earth, kieselguhr, diatomaceous earth, montmorillonite, the permutites, and the like; the various treated clays and clay-like materials, such as Tonsil, Celite, Sil-O-Cel, Terrana and the like; and artificially prepared materials, such as Activated Alumina, silica gel, the artificial permutites, and the like. The aluminum halide may, moreover, be simply suspended in the liquid reaction mixture, or it may be employed in the form of a complex double compound such, for instance, as those known as "Gustavson's compounds" (C. **1903,** II, 1113) and the "Ansolvo Acids" (*Ann.*, **455,** 227-253).

"The isomerization is executed, according to the process of the present invention, under a pressure of hydrogen. It is found that hydrogen exerts a remarkable and unexpected influence in the isomerization reaction and that an appreciable pressure of hydrogen is, in general, very beneficial. By the use of suitable pressure of hydrogen, higher temperatures affording more practical reaction rates may be employed, undesirable side reactions are repressed, and the active life of the catalyst is materially increased.

"It is also found that moderate hydrogen pressures, *i.e.*, from about one to about five atmospheres (measured at 20° C.), tend to a certain extent to promote the isomerizing activity of the catalyst. Thus, whereas unpromoted aluminum halides are known not to catalyze isomerization to any appreciable extent, it is found that, in the case of the isomerization of normal butane and normal pentane, the isomerization may be effected even in the absence of a hydrogen halide if a suitable pressure of hydrogen is applied."

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